Topology and Phase Transitions: Theorem on a necessary relation

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Abstract

We prove a theorem that establishes a necessary topological condition for the occurrence of first or second order phase transitions; in order for these to occur, the topology of certain submanifolds of configuration space must necessarily change at the phase transition point. The theorem applies to a wide class of smooth, finite-range and confining potentials $V$ bounded below, describing systems confined in finite regions of space with continuously varying coordinates. The relevant configuration space submanifolds are the level sets $\{\Sigma_v := V_N^{-1}(v)\}_{v \in \mathbb{R}}$ of the potential function $V$, $N$ is the number of degrees of freedom and $v$ is the potential energy. The proof proceeds by showing that, under the assumption of diffeomorphism of the equipotential hypersurfaces $\{\Sigma_v\}_{v \in \mathbb{R}}$ in an arbitrary interval of values for $v$, the Helmholtz free energy is uniformly convergent in $N$ to its thermodynamic limit, at least within the class of twice differentiable functions, in the corresponding interval of temperature.

1 Introduction

In Statistical Mechanics, a central task of the mathematical theory of phase transitions has been to prove the loss of differentiability of the pressure function – or of other thermodynamic functions – with respect to temperature, or volume, or an external field. The first rigorous result of this kind is the well known Yang-Lee theorem showing that, despite the smoothness of the grand canonical
partition function, in the \( N \to \infty \) limit also piecewise differentiability of pressure or other thermodynamic functions becomes possible.

Another approach to the problem has considerably grown after the introduction of the concept of a Gibbs measure for infinite systems by Dobrushin, Lanford and Ruelle. In this framework, the phenomenon of phase transition is seen as the consequence of non-uniqueness of a Gibbs measure for a given type of interaction among the particles of a system [2, 3].

Recently, it has been conjectured that the origin of the phase transition singularities could be attributed to suitable topology changes within the family of equipotential hypersurfaces \( \{ \Sigma_v = V^{-1}(v) \} \) of configuration space. These level sets of \( V \) naturally foliate the support of the statistical measures (canonical or microcanonical) so that the mentioned topology change would induce a change of the measure itself at the transition point [4, 5, 6, 7]. In a few particular cases, the truth of this topological hypothesis has been given strong evidence: i) through the numerical computation of the Euler characteristic for the \( \{ \Sigma_v \} \) of a two-dimensional lattice \( \varphi^4 \) model [8]; ii) through the exact analytic computation of the Euler characteristic of \( \{ M_v = V^{-1}(v, -\infty) \} \) submanifolds of configuration space for two different models [9, 10].

In the present paper, for a whole class of physical potentials (specified in Section 2), we prove the topological hypothesis by proving the following

**Theorem.** Let \( V_N(q_1, \ldots, q_N) : \mathbb{R}^N \to \mathbb{R} \) be a smooth, non-singular, finite-range potential. Denote by \( \Sigma_v := V^{-1}(v) \), \( v \in \mathbb{R} \), its level sets, or equipotential hypersurfaces, in configuration space, and denote by \( \mathcal{F}_N = \{ \Sigma_v \} \) the family of these level sets. Then let \( \bar{v} = v/N \) be the potential energy per degree of freedom.

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 \( N > N_0 \) it is

\[
\Sigma_{N\bar{v}} \approx \Sigma_{N\bar{v}'}
\]

that is \( \Sigma_{N\bar{v}} \) is diffeomorphic to \( \Sigma_{N\bar{v}'} \), then the sequence of the Helmoltz free energies \( \{ F_N(\beta) \} \) 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 \( C^2(I_\beta) \) so that \( F_\infty \in C^2(I_\beta) \) and neither first nor second order phase transitions can occur in the (inverse) temperature interval \( (\beta(\bar{v}_0), \beta(\bar{v}_1)) \).

This is our Main Theorem given in Section 3.

This theorem means that a topology change of the \( \{ \Sigma_v \} \) at some \( v_c \) is a necessary condition for a phase transition to take place at the corresponding energy or temperature value.

The converse is not true. As we point out in Remark 3, the above mentioned works in Refs. [6] and [9, 10] provide some hints about the sufficiency conditions.
2 Basic definitions

For a physical system $S$ of $n$ particles confined in a bounded subset $\Lambda$ of $\mathbb{R}^d$, $d = 1, 2, 3$, and interacting through a real valued potential function $V$ defined on $\Lambda \times N$, where $N = nd$, the configurational microcanonical volume $\Omega(v, N)$ is defined for any value $v$ of the potential $V$ as

$$\Omega(v, N) = \int_{\Lambda \times N} dq_1 \ldots dq_N \delta[V(q_1, \ldots, q_N) - v] = \int_{\Sigma_v} \frac{d\sigma}{\|\nabla V\|}, \quad (1)$$

where $d\sigma$ is a surface element of $\Sigma_v := V^{-1}(v)$; in what follows $\Omega(v, N)$ is also called structure integral. The norm $\|\nabla V\|$ is defined as $\|\nabla V\| = \left(\sum_{i=1}^{N} (\partial_{q_i} V)^2\right)^{1/2}$.

The configurational partition function $Z_c(\beta, N)$ is defined as

$$Z_c(\beta, N) = \int_{\Lambda^N} dq_1 \ldots dq_N \exp[-\beta V(q_1, \ldots, q_N)] = \int_0^\infty dv \int_{\Sigma_v} \frac{d\sigma}{\|\nabla V\|}, \quad (2)$$

where the real parameter $\beta$ has the physical meaning of an inverse temperature.

Notice that the formal Laplace transform of the structure integral in the r.h.s. of (2) stems from a co-area formula [15] which is of very general validity (it holds also for Hausdorff measurable sets).

Now we can define the configurational thermodynamic functions to be used in this paper.

**Definition 1** Using the notation $\bar{v} = v/N$ for the value of the potential energy per particle, we introduce the following functions:

- Configurational microcanonical entropy. For any $N \in \mathbb{N}$ and $\bar{v} \in \mathbb{R}$,

  $$S_N(\bar{v}) \equiv S_N(\bar{v}; V) = \frac{1}{N} \log \Omega(N\bar{v}, N).$$

- Configurational canonical free energy. For any $N \in \mathbb{N}$ and $\beta \in \mathbb{R}$,

  $$f_N(\beta) \equiv f_N(\beta; V) = \frac{1}{N} \log Z_c(\beta, N).$$

- Configurational canonical quasi-entropy given as the Legendre transform of the configurational canonical free energy, $f_N$, $N \in \mathbb{N}$ and for any $\bar{v} \in \mathbb{R}$,

  $$S_N^{(-)}(\bar{v}) = \sup_{\beta} \{f_N(\beta) + \beta \cdot \bar{v}\}, \quad \tag{3}$$

but rigorous results are not yet available.
yielding, for any $N \in \mathbb{N}$ and $\bar{v} \in \mathbb{R}$,

$$S_N^{(-)}(\bar{v}) = f_N(\beta_N) + \beta_N \cdot \bar{v}$$

(4)

with, for any $N \in \mathbb{N}$ and $\bar{v} \in \mathbb{R}$,

$$\beta_N(\bar{v}) = \frac{\partial S_N^{(-)}}{\partial \bar{v}}(\bar{v}),$$

(5)

and the inverse relation, valid for any $N \in \mathbb{N}$ and $\beta \in \mathbb{R}$,

$$v(\beta) = -\frac{\partial f_N}{\partial \beta}(\beta).$$

(6)

Finally, for a system described by a Hamiltonian function $H$ of the kind $H = \sum_{i=1}^{N} p_i^2/2 + V(q_1, \ldots, q_N)$, the Helmoltz free energy is defined by

$$F_N(\beta; H) = -(N\beta)^{-1} \log \int d^N p \, d^N q \, \exp[-\beta H(p, q)],$$

(7)

whence

$$F_N(\beta; H) = -(2\beta)^{-1} \log(\pi/\beta) - f_N(\beta, V)/\beta$$

(8)

and its thermodynamic limit ($N \to \infty$ and $\text{vol}(\Lambda^{xN})/N = \text{const}$)

$$F_{\infty}(\beta) = \lim_{N \to \infty} F_N(\beta; H).$$

(9)

**Definition 2 (First and second order phase transitions)** We say that a physical system $S$ undergoes a phase transition if there exists a thermodynamic function which – in the thermodynamic limit ($N \to \infty$ and $\text{vol}(\Lambda^{xN})/N = \text{const}$) – is only piecewise analytic. In particular, if the first-order derivative of the Helmoltz free energy $F_{\infty}(\beta)$ is discontinuous at some point $\beta_c$, then we say that a first-order phase transition occurs. If the second-order derivative of the Helmoltz free energy $F_{\infty}(\beta)$ is discontinuous at some point $\beta_c$, then we say that a second-order phase transition occurs.

**Definition 3 (Standard potential)** We say that an $N$ degrees of freedom potential $V_N$ is a standard potential if it is of the form

$$V_N : \quad B(N) \subset \mathbb{R}^N \to \mathbb{R}$$

$$V_N(q) = \sum_{\alpha, \gamma = 1}^{N} C_{\alpha \gamma} \Psi(||\bar{q}_\alpha - \bar{q}_\gamma||) + \sum_{\alpha = 1}^{N} \Phi(||\bar{q}_\alpha||)$$

(10)
where \((\Psi, \Phi)\) are real valued functions of one variable, and where the coefficients \(C_{\alpha\gamma}\) are such that additivity holds. By additivity we mean what follows. Consider two systems \(S_1\) and \(S_2\), having \(N_1\) and \(N_2\) degrees of freedom, occupying volumes \(\Lambda_1\) and \(\Lambda_2\), having potential energies \(v_1\) and \(v_2\), for any \((q_1, \ldots, q_{N_1}) \in \Lambda_1^{\times N_1}\) such that \(V_{N_1}(q_1, \ldots, q_{N_1}) = v_1\), for any \((q_{N_1+1}, \ldots, q_{N_1+N_2}) \in \Lambda_2^{\times N_2}\) such that \(V_{N_2}(q_{N_1+1}, \ldots, q_{N_1+N_2}) = v_2\), for \((q_1, \ldots, q_{N_1+N_2}) \in \Lambda_1^{\times N_1} \times \Lambda_2^{\times N_2}\) let \(V_N(q_1, \ldots, q_{N_1+N_2}) = v\) be the potential energy of the compound system \(S = S_1 + S_2\) which occupies the volume \(\Lambda = \Lambda_1 \cup \Lambda_2\) and contains \(N = N_1 + N_2\) degrees of freedom. If

\[
v(N_1 + N_2, \Lambda_1 \cup \Lambda_2) = v_1(N_1, \Lambda_1) + v_2(N_2, \Lambda_2) + v'(N_1, N_2, \Lambda_1, \Lambda_2) \tag{11}\]

where \(v'\) stands for the interaction energy between \(S_1\) and \(S_2\), and if \(v'/v_1 \to 0\) and \(v'/v_2 \to 0\) for \(N \to \infty\) then \(V_N\) is additive.

**Definition 4 (Short-range potential)** In defining a short-range potential, a distinction has to be made between lattice systems (solids) and fluid systems (gases and liquids). Given a standard potential \(V\) on a lattice, we say that it is a short-range potential if the coefficients \(C_{\alpha\gamma}\) are such that for any \(\alpha, \gamma = 1, \ldots, N\), 
\[
C_{\alpha\gamma} = 0 \quad \text{iff} \quad |\alpha - \gamma| > c,
\]
with \(c\) is definitely constant for \(N \to \infty\).

Given a standard potential \(V\) for a fluid system, we say that it is a short-range potential if there exist \(R_0 > 0\) and \(\epsilon > 0\) such that for \(|q| > R_0\) it is \(|\Psi(|q|)| < |q|^{-(d+1+\epsilon)}\), where \(d = 1, 2, 3\) is the spatial dimension.

**Definition 5 (Stable potential)** We say that a potential \(V_N\) is stable \([11]\) if there exists \(B \geq 0\) such that

\[
V_N(q_1, \ldots, q_N) \geq -NB \tag{12}
\]

for any \(N > 0\) and \((q_1, \ldots, q_N) \in \Lambda^{\times N}\).

**Definition 6 (Confining potential)** If \(\Lambda = \mathbb{R}^d\), a standard potential \(V\) is said to be a confining potential when \(V(q) \to \infty\) whenever \(|q_\alpha| \to \infty\) or \(|q_\alpha - q_\gamma| \to \infty\). This means that at finite potential energy no particle can escape arbitrarily far away.

**Remark 1 (Compactness of equipotential hypersurfaces)** From the previous definition it follows that, for a confining potential, the equipotential hypersurfaces \(\Sigma_v\) are compact (because they are closed by definition and bounded in view of particle confinement).
Proposition 1 (Pointwise convergence) Assume $V_N$ is a standard, confining, short-range and stable potential. Assume also that there exists $N_0 \in \mathbb{N}$ such that $\bigcap_{N>N_0}^{\infty} \text{dom}(S_N^{(-)})$ and $\bigcap_{N>N_0}^{\infty} \text{dom}(S_N)$ are nonempty sets, then the following pointwise limits exist almost everywhere

$$\lim_{N \to \infty} S_N^{(-)}(\bar{v}) \equiv S^{(-)}(\bar{v}) \quad \text{for} \quad \bar{v} \in \bigcap_{N>N_0}^{\infty} \text{dom}(S_N^{(-)})$$

and

$$\lim_{N \to \infty} S_N(\bar{v}) \equiv S(\bar{v}) \quad \text{for} \quad \bar{v} \in \bigcap_{N>N_0}^{\infty} \text{dom}(S_N)$$

and moreover

$$S^{(-)}(\bar{v}) = S(\bar{v}) \quad \text{for} \quad \bar{v} \in \bigcap_{N>N_0}^{\infty} \text{dom}(S_N^{(-)}) \cap \bigcap_{N>N_0}^{\infty} \text{dom}(S_N)$$

Proof. The existence of the thermodynamic limit for the sequences of functions $S_N^{(-)}$ and $S_N$, associated with a standard potential function $V_N$ with short-range interactions, stable and confining is formally proved in [11].

To prove that in the thermodynamic limit the two entropies $S^{(-)}$ and $S$ are equal one proceeds as follows.

By definition, $Z_c(\beta, N)$ is the Laplace transform of the structure integral $\Omega(v, N)$. The inverse transform gives

$$\Omega(v, N) = \frac{1}{2\pi i} \int_{\beta' - i\infty}^{\beta' + i\infty} Z_c(\beta, N)e^{\beta v} d\beta$$

$$= \frac{1}{2\pi} \int_{-\infty}^{+\infty} \exp\{\log(Z_c(\beta' + i\beta'', N)) + (\beta' + i\beta'')v\} d\beta'' , \quad (13)$$

where the integration is performed along the line of the complex plane which is orthogonal to the real axis and crosses it at the point $(\beta', 0)$, where $\beta'$ is a real number greater than $\lambda_0$, the abscissa of uniform convergence of the Laplace transform. As the argument of the integral in the r.h.s. of Eq. (13) is a complex exponential of terms depending upon $N$ ($v$ and $\log Z_c$), in the limit of arbitrarily large $N$, its contribution to the integral comes from its maximum. If $\beta_N^*$ denotes the value of $\beta$ which corresponds to the largest value of the integrand, $\beta_N^*$ is then defined through the equations

$$\left( \frac{\partial \log Z_c}{\partial \beta''}(\beta' + i\beta'') \right)_{\beta_N^*} + iv = 0 , \quad \left( \frac{\partial^2 \log Z_c}{\partial (\beta'')^2}(\beta' + i\beta'') \right)_{\beta_N^*} < 0 . \quad (14)$$
As $\beta' > \lambda_0$, the function $\log Z_c$ is holomorphic and satisfies the Cauchy-Riemann conditions, thus the Eqs. (14) can be rewritten as

$$\left( \frac{\partial \log Z_c}{\partial \beta'}(\beta' + i\beta'') \right)_{\beta_N^*} + v = 0 \, , \quad \left( \frac{\partial^2 \log Z_c}{\partial \beta'^2}(\beta' + i\beta'') \right)_{\beta_N^*} > 0.$$ 

The first equation indicates that $\beta_N^*$ is a real number. The second equation is the maximum condition for a stationary point, and it is satisfied because $\partial^2 \log Z_c(\beta) = \langle (V^2)_c - \langle V \rangle_c \rangle > 0$, where $\langle \cdot \rangle_c$ stands for averaging with the canonical partition function, and $\partial \beta = \partial / \partial \beta$.

Thus $\beta_N^*$ is a maximum point, so that we can Taylor expand the exponent in the integral (13) as follows

$$\log Z_c(\beta' + i\beta'') + (\beta' + i\beta'')v \simeq \log Z_c(\beta_N^*) + (\beta_N^*)v + \frac{1}{2} \frac{\partial^2 \log Z_c}{\partial \beta''^2}(\beta_N^*) \cdot (\beta'')^2 + \cdots \quad (15)$$

Then the structure integral then can be written as

$$\Omega(v,N) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \exp \left[ \log Z_c(\beta_N^*,N) + \beta_N^*v - \frac{1}{2} \frac{\partial^2 \log Z_c}{\partial \beta''^2}(\beta_N^*,N) \cdot (\beta'')^2 + \cdots \right] d\beta''$$

leading to the approximate relation

$$\frac{1}{N} \log \Omega(v,N) \simeq \frac{1}{N} \log Z_c(\beta_N^*,N) + \beta_N^*v - \frac{1}{2N} \log \left( \frac{1}{2\pi} \frac{\partial^2 \log Z_c}{\partial \beta''^2}(\beta_N^*,N) \right) ,$$ 

that is $S_N(v) = S_N^{(-)}(v) + \text{remainder}$ (with the notations of the Definition 1). In the pointwise limit ($N \to \infty$) performed at any $\bar{v} = v/N$ and $N \to \infty$, this approximate relation becomes exact

$$\lim_{N \to \infty} \left[ \frac{1}{N} \log \Omega(N\bar{v},N) \right] = \lim_{N \to \infty} \left[ \frac{1}{N} \log Z_c(\beta_N^*,N) \right] + \beta_{\infty}^*\bar{v} \quad (16)$$

where $\bar{v} := v/N$ and $\beta_{\infty}^* = \lim_{N \to \infty} \beta_N^*$. Whence

$$\forall \bar{v} \in \mathbb{R}, \quad S(\bar{v}) = S^{(-)}(\bar{v}) \, . \quad (17)$$

$\square$
Proposition 2 (Pointwise convergence) Assume \(V_N\) is a standard, confining, short-range and stable potential. Assume also that there exists \(N_0 \in \mathbb{N}\) such that \(\bigcap_{N>N_0} \text{dom}(f_N)\) and \(\bigcap_{N>N_0} \text{dom}(\beta_N)\) are nonempty, then the following limits exist pointwise almost everywhere

\[
\lim_{N \to \infty} f_N(\beta) \equiv f(\beta), \quad \text{for } \beta \in \bigcap_{N>N_0} \text{dom}(f_N)
\]

\[
\lim_{N \to \infty} \beta_N(\bar{v}) \equiv \beta(\bar{v}), \quad \text{for } \bar{v} \in \bigcap_{N>N_0} \text{dom}(\beta_N).
\] (18)

Proof. See Ref. [11].

3 Main Theorem

In this Section we prove our Main Theorem which is enunciated as follows:

Theorem 1 Let \(V_N\) be a standard, smooth, confining, short-range potential bounded from below (Definitions 3, 4, 5 and 6)

\[
V_N : \quad B(N) \subset \mathbb{R}^N \to \mathbb{R}
\]

\[
V_N(q) = \sum_{\langle \alpha, \gamma \rangle} \Psi(\|\bar{q}_\alpha - \bar{q}_\gamma\|) + \sum_\alpha \Phi(\|q_\alpha\|).
\] (19)

Let \((\Psi, \Phi)\) be real valued one variable functions, let \(\langle \alpha, \gamma \rangle\) label interacting pairs of degrees of freedom within a short-range, and let \(\mathcal{F}_N = \{\Sigma_v\}_{v \in \mathbb{R}}\) be the family of \(N - 1\)-dimensional equipotential hypersurfaces \(\Sigma_v := V_N^{-1}(v), v \in \mathbb{R}, \text{ of } \mathbb{R}^N\).

Let \(\bar{v}_0, \bar{v}_1 \in \mathbb{R}, \bar{v}_0 < \bar{v}_1\). If there exists \(N_0\) such that for any \(N > N_0\) and for any \(v, v' \in I_0 = [\bar{v}_0, \bar{v}_1]\)

\[
\Sigma_{N_0} \text{ is } C^\infty - \text{diffeomorphic to } \Sigma_{N_0'},
\]

(notation: \(\Sigma_{N_0} \approx \Sigma_{N_0'}\)) then the limit entropy \(S(\bar{v})\) is of differentiability class \(C^3(I_0)\), and, consequently, \(\beta(\bar{v})\) belongs to \(C^2(I_0)\), whence the limit Helmholtz free energy function \(F_\infty \in C^2(\overset{\circ}{I}_\beta)\), where \(\overset{\circ}{I}_\beta\) denotes open interior of \(\beta([\bar{v}_0, \bar{v}_1])\), so that the system described by \(V\) has neither first nor second order phase transitions in the inverse-temperature interval \(\overset{\circ}{I}_\beta\).

The idea of the proof of the Main Theorem is the following. In order to prove that a topology change of the equipotential hypersurfaces \(\Sigma_v\) of configuration
space is a necessary condition for a thermodynamic phase transition to occur, we shall prove the equivalent proposition that if any two hypersurfaces \( \Sigma_v \) and \( \Sigma_{v'} \) with \( v, v' \in (a, b) \) are diffeomorphic then no phase transition can occur in the (inverse) temperature interval \((\beta(a), \beta(b))\). To this purpose we have to show that, in the limit \( N \to \infty \) and \( \text{vol}(\Lambda)/N = \text{const} \), the Helmholtz free energy \( F_N(\beta; H) \) is at least twice differentiable as a function of \( \beta = 1/T \) in the interval \((\beta(a), \beta(b))\). For the standard Hamiltonian systems that we consider throughout this paper, this is equivalent to show that the sequence of configurational free energies \( \{f_N(T; H)\}_{N \in \mathbb{N}^+} \) is uniformly convergent at least in \( C^2 \) so that also \( \{f_\infty(T; H)\} \in C^2 \).

We shall give the proof of the Main Theorem through the following Lemmas which are separately proven in subsequent Sections.

**Lemma 1 (Absence of critical points)** Let \( f : M \to [a, b] \) a smooth map on a compact manifold \( M \) with boundary. Suppose \( f(\partial M) = \{a, b\} \) and that for any \( c, d \in [a, b] \) it is \( f^{-1}(c) \approx f^{-1}(d) \), that is all the level surfaces of \( f \) are diffeomorphic. Then \( f \) has no critical points, that is \( \nabla f \geq C > 0 \), in \([a, b]\); \( C \) is a constant.

*Proof.* The proof of this Lemma is given in Section 4.

**Lemma 2 (Smoothness of the structure integral)** Let \( V_N \) be a standard, short-range, stable and confining potential function bounded below. Let \( F_N = \{\Sigma_v\}_{v \in \mathbb{R}} \) be the family of \((N-1)\)-dimensional equipotential hypersurfaces \( \Sigma_v := V_N^{-1}(v), v \in \mathbb{R}, \) of \( \mathbb{R}^N \), then we have:

If for any \( v, v' \in [v_0, v_1] \), \( \Sigma_v \approx \Sigma_{v'} \) then \( \Omega(v, N) \in C^\infty([v_0, v_1]) \).

*Proof.* The proof of this Lemma is given in Section 5.

**Lemma 3 (Uniform convergence)** Let \( U \) and \( U' \) be two open intervals of \( \mathbb{R} \). Let \( h_N \) be a sequence of functions from \( U \) to \( U' \), differentiable on \( U \), and let \( h : U \rightarrow U' \) be such that for any \( x \in U \), \( \lim_{N \to \infty} h_N(x) = h(x) \). Let \( a \in U \), if there exists \( M \in \mathbb{R} \) such that for any \( N \in \mathbb{N} \) it is \( \left| \frac{dh_N}{dx}(a) \right| \leq M \), then \( h \) is continuous at \( a \).

*Proof.* The proof of this Lemma simply follows from the Ascoli theorem on equicontinuous sets of applications [13].
Lemma 4 (Uniform upper bounds) Let $V_N$ be a standard, short-range, stable and confining potential function bounded below. Let $\mathcal{F}_N = \{\Sigma_v \}_{v \in \mathbb{R}}$ be the family of $(N - 1)$-dimensional equipotential hypersurfaces $\Sigma_v := V_N^{-1}(v)$, $v \in \mathbb{R}$, of $\mathbb{R}^N$, if

$$\text{for any } N, \text{ for any } \bar{v}, \bar{v}' \in I_\theta = [\bar{v}_0, \bar{v}_1], \quad \Sigma_{N\bar{v}} \approx \Sigma_{N\bar{v}'}$$

then

$$\sup_{N, \bar{v} \in I_\theta} |S_N(\bar{v})| < \infty \quad \text{and} \quad \sup_{N, \bar{v} \in I_\theta} \left| \frac{\partial^k S_N}{\partial \bar{v}^k}(\bar{v}) \right| < \infty, \quad k = 1, 2, 3, 4.$$  

Proof. The proof of this Lemma is given in Section 6.

Proof. Under the hypothesis that all the level surfaces of $V_N$ are diffeomorphic in the interval $I_\theta$ we know from Lemma 1 that there are no critical points of $V_N$ in $I_\theta$, i.e. there exists $C(N) > 0$ such that for any $N > N_0$

$$\text{for } \bar{v} \in I_\theta, \text{ and for any } x \in \Sigma_{N\bar{v}}, \quad \|\nabla V_N(x)\| \geq C > 0. \quad (20)$$

Therefore, the restriction of $V_N$

$$\tilde{V}_N = V_{|V_N^{-1}(I_{N\bar{v}}) : V_N^{-1}(I_{N\bar{v}}) \subset B \to \mathbb{R}} \quad (21)$$

always defines a Morse function, since $V_N$ is bounded below. Notice that

$$S_N(\bullet ; V_N)_{I_{\bar{v}}} = S_N(\bullet ; \tilde{V}_N)_{I_{\bar{v}}}, \quad (22)$$

in what follows we shall drop the tilde and $V_N$ will denote the above given restriction.

Now, since the condition (20) holds for the hypersurfaces $\{\Sigma_{N\bar{v}}\}_{\bar{v} \in I_\theta}$, from Lemma 2 it follows that for any $N > N_0$, $\Omega(N\bar{v}, N)$ is actually in $C^\infty(I_{\bar{v}})$, where $I_{\bar{v}} = (\bar{v}_0, \bar{v}_1)$; this implies that for any $N > N_0$, also $S_N$ belongs to $C^\infty(I_{\bar{v}})$.

While at any finite $N$ – under the main assumption of the theorem – the entropy functions $S_N$ are smooth, we do not know what happens in the $N \to \infty$ limit. To know the behaviour at the limit, we have to prove the uniform convergence of the sequence $\{S_N\}_{N \in \mathbb{N}^+}$. Lemmas 3 and 4 prove exactly that this sequence is uniformly convergent at least in the space $C^3(I_{\bar{v}})$, so that we can conclude that also $S \in C^3(I_{\bar{v}})$.

As $S = S^{(-)}$ in $I_\theta$ (Proposition 1), also $S^{(-)}$ lies in $C^3(I_{\bar{v}})$ and $\beta$ in $C^2(I_{\bar{v}})$.  

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Moreover, by definition and existence of the uniform limit of \( \{S_N\}_{N \in \mathbb{N}_+} \), for any \( \bar{v} \in I_\beta \) we can write

\[
S(\bar{v}) = f(\beta(\bar{v})) + \beta(\bar{v}) \cdot \bar{v}
\]

which entails \( f \in C^2(\beta(I_\beta)) \equiv C^2(I_\beta) \).

Since the kinetic energy term of the Hamiltonian describing the system \( S \) gives only a smooth contribution, also the Helmoltz free energy \( F_\infty \) has differentiability class \( C^2(I_\beta) \). Hence we conclude that the system \( S \) does not undergo neither first nor second order phase transitions in the inverse-temperature interval \( \beta \in I_\beta \). □

**Remark 2 (Domain of physical applications)** Notice that the requirement of standard, stable, confining and short-range potentials \( V_N \) is not very restrictive in view of the physical relevance of the theorem. In fact, the interatomic and intermolecular interaction potentials (like Lennard-Jones, Morse, van der Waals potentials) which are typically encountered in condensed matter theory, as well as classical spin potentials, fulfil these requirements.

**Remark 3 (Sufficiency conditions)** Notice that the converse of this theorem is not true. In fact, consider for example a one dimensional lattice of classical spins (or of coupled rotators) described by the potential function \( V_N(q) = \sum_{i=1}^{N} [1 - \cos(q_{i+1} - q_i)] \): it has many critical points \([9]\) so that its level sets \( \{\Sigma_v\}_{v \in \mathbb{R}} \) undergo many topological changes, however, since no phase transition is associated with this potential, none of these topological changes corresponds to a phase transition. Therefore we deduce that, while the loss of diffeomorphicity – thus a topology change of the \( \{\Sigma_v\}_{v \in \mathbb{R}} \) at some \( v_c \) – is necessary for the occurrence of a phase transition, further hypotheses about the kind of topology changes that entail the appearance of a phase transition are needed. Though this problem of sufficiency is still wide open, we already have some useful hints provided by the exact analytic computation of the Euler characteristic of the submanifolds \( M_v = \{q_1, \ldots, q_N \in \Lambda| V(q_1, \ldots, q_N) \leq v\} \) for two models undergoing first or second order phase transitions or no phase transitions at all\([4, 10]\). These results, together with the numerically computed Euler characteristic \( \chi(\Sigma_v) \) vs. \( v \) for a two-dimensional lattice \( \varphi^4 \) model undergoing a symmetry-breaking phase transition \([1]\), suggest that phase transitions would correspond to abrupt transitions in the way topology changes as a function of \( v \). In the so-called mean-field \( XY \) model, for example, the phase transition stems from the simultaneous attachment of handles of \( O(N) \) different types on the same critical level \([4]\).
## 4 Proof of Lemma 1, absence of critical points

Since \( f \) is a good Morse function, let us consider the case of the existence of at least one critical value \( c \in [a, b] \) so that \( \nabla f = 0 \) at some points of the level set \( f^{-1}(c) \). The set of critical points \( \sigma(c) = \{ x^{i,k}_c \in f^{-1}(c) | (\nabla f)(x^{i,k}_c) = 0 \} \) is a point set \([12]\), the index \( i \) labels the different critical points and \( k_i \) is the Morse index of the \( i \)-th critical point. After the “non-critical neck” theorem \([12]\), we know that the level sets \( f^{-1}(v) \) with \( v \in [a, c - \varepsilon] \) and arbitrary \( \varepsilon > 0 \) are diffeomorphic because no critical point exists in the interval \([a, c - \varepsilon]\). Now, in the neighborhood of each critical point \( x^{i,k}_c \), the existence of the Morse chart \([13]\) allows to represent the function \( f \) as follows

\[
\begin{align*}
  f(x) = f(x^{i,k}_c) - x_1^2 - \cdots - x_k^2 + x_{k+1}^2 + \cdots + x_n^2.
\end{align*}
\]

(23)

Let us define the \( i \)-th critical ball \( B^i_\eta(x^{i,k}_c) \) of radius \( \eta > 0 \) to be the set of points whose euclidean distance from \( x^{i,k}_c \) does not exceed \( \eta \), and shaped so as its boundary \( \partial B^i_\eta(x^{i,k}_c) \) has the property that, for \( v, v' \in [a, b] \), \( \partial(f^{-1}(v) \cap B^i_\eta(x^{i,k}_c)) \) is mapped diffeomorphically to \( \partial(f^{-1}(v') \cap B^i_\eta(x^{i,k}_c)) \) through the standard flow \([13]\) of the vector field \( X = -\nabla f/\|\nabla f\|^2 \). Then for any \( v, v' \in [a, c - \varepsilon] \) with arbitrary \( \varepsilon > 0 \) from Eq.(23) it follows that

\[
(f^{-1}(v) \cap B^i_\eta(x^{i,k}_c)) \approx (f^{-1}(v') \cap B^i_\eta(x^{i,k}_c))
\]

(24)

which could not be otherwise because \( f^{-1}(v') \approx f^{-1}(v) \), whereas for any \( v \in [a, c - \varepsilon] \) with arbitrary \( \varepsilon > 0 \), and for any \( x^{i,k}_c \in \sigma(c) \)

\[
(f^{-1}(v) \cap B^i_\eta(x^{i,k}_c)) \not\approx (f^{-1}(c) \cap B^i_\eta(x^{i,k}_c))
\]

(25)

because the quadrics in (23) are degenerate at the critical value \( c \). Hence for any \( v < c \)

\[
\begin{align*}
  f^{-1}(v) \not\approx f^{-1}(c).
\end{align*}
\]

(26)

Thus, if for any pair of values \( v, v' \in [a, b] \) one has \( f^{-1}(v') \approx f^{-1}(v) \), no critical point of \( f \) can exist in the interval \([a, b]\). □

## 5 Proof of Lemma 2, smoothness of the structure integral

We make use of the following Lemma
Lemma 5 Let $U$ be a bounded open subset of $\mathbb{R}^N$, let $\psi$ be a Morse function defined on $U$, $\psi : U \subset \mathbb{R}^N \rightarrow \mathbb{R}$ and $\mathcal{F} = \{\Sigma_v\}_{v}$ the family of hypersurfaces defined as $\Sigma_v = \{x \in U|\psi(x) = v\}$, then we have:

if for any $v, v' \in [v_0, v_1]$, $\Sigma_v \approx \Sigma_v'$

then, for any $g \in C^\infty(U)$, $\int_{\Sigma_v} g \, d\sigma$ is $C^\infty$ in $[v_0, v_1]$.

Proof. To prove this Lemma we need the following Theorem[15, 16]:

Theorem 2 (Federer, Laurence) Let $O \subset \mathbb{R}^p$ be a bounded open set. Let $\psi \in C^{n+1}(\bar{O})$ be constant on each connected component of the boundary $\partial O$ and $g \in C^n(O)$.

By introducing $O_{t,v} = \{x \in O \mid t < \psi(x) < t'\}$, and $F(v) = \int_{\{\psi=v\}} g \, d\sigma^{p-1}$, where $d\sigma^{p-1}$ represents the Lebesgue measure of dimension $p-1$.

If $C > 0$ exists such that for any $x \in O_{t',v}$, $|\nabla \psi(x)| \geq C$, for any $k \leq n$, for any $v \in ]t,t']$, one has

$$\frac{d^k F}{dv^k}(v) = \int_{\{\psi=v\}} A^k g \, d\sigma^{p-1}.$$  

with $A^k g = \nabla \left( \frac{\nabla \psi}{|\nabla \psi|} g \right) \frac{1}{|\nabla \psi|}$.

By applying this Theorem to the function $\psi$ of the Lemma we have that, if there exists a constant $C > 0$ such that for any $x \in O_{v_0,v_1}$ it is $|\nabla \psi(x)| \geq C$, then

$$\frac{d^k F}{dv^k}(v) = \int_{\Sigma_v} A^k g \, d\sigma, \forall v \in ]v_0, v_1[.$$  

Now, under the hypothesis that for any $v, v' \in [v_0, v_1]$, $\Sigma_v \approx \Sigma_v'$, we know from Lemma[17] “absence of critical points”, that this hypothesis is equivalent to the assumption that for any $v \in [v_0, v_1]$, $\Sigma_v$ has no critical points. Hence there exists a constant $C > 0$ such that $\forall x \in O_{v_0,v_1} |\nabla \psi(x)| \geq C$. Furthermore, as $|\nabla \psi|$ is strictly positive, $A$ is a continuous operator on $O_{v_0,v_1}$. Thus, being $\Sigma_v$ compact, $\frac{d^k F}{dv^k}$ is continuous on the interval $]v_0, v_1[$, $\forall k$, namely $\int_{\Sigma_v} g d\sigma \in C^\infty([v_0, v_1])$.

To conclude the proof of the Lemma we have to use Lemma taking $\psi = V_N$ and $g = 1/|\nabla V_N|$, assuming that $V_N$ is a Morse function and that $|\nabla V_N|$ is strictly positive (absence of critical points of $V_N$ stemming from the hypothesis of diffeomorphicity of the Main Theorem). □
6 Proof of Lemma 4, upper bounds

The proof of this Lemma is splitted into two parts. In part A some preliminary results to be used in part B are given, and in part B the inequalities of the Lemma are proved.

6.1 Part A

We begin by showing that on any \((N - 1)\)-dimensional hypersurface \(\Sigma_{N\bar{v}} = V_N^{-1}(N\bar{v}) = \{X \in \mathbb{R}^N \mid V_N(X) = N\bar{v}\}\) of \(\mathbb{R}^N\), we can define a homogeneous non-periodic random Markov chain whose probability measure is the configurational microcanonical measure, namely \(d\sigma/\|\nabla V_N\|\).

Notice that at any finite \(N\) and in the absence of critical points of the potential \(V_N\) (because of \(\|\nabla V_N\| \geq C > 0\)) the microcanonical measure is smooth. The microcanonical averages \(\langle \rangle_{\mu_c}^{\Sigma_{N\bar{v}}}\) are then equivalently computed as “time” averages along the previously mentioned Markov chains.

In the following, when no ambiguity is possible, for the sake of notation we shall drop the suffix \(N\) of \(V_N\).

**Lemma 6** On each finite dimensional level set \(\Sigma_{N\bar{v}} = V_N^{-1}(N\bar{v})\) of a standard, smooth, confining, short range potential \(V\) bounded below, and in the absence of critical points, there exists a random Markov chain of points \(\{X_i \in \mathbb{R}^N\}_{i \in \mathbb{N}_+}\), constrained by the condition \(V(X_i) = N\bar{v}\), which has

\[
\frac{d\mu}{\|\nabla V\|} = \left(\int_{\Sigma_{N\bar{v}}} \frac{d\sigma}{\|\nabla V\|}\right)^{-1}
\]

as its probability measure, so that, for a smooth function \(F: \mathbb{R}^N \rightarrow \mathbb{R}\) it is

\[
\left(\int_{\Sigma_{N\bar{v}}} \frac{d\sigma}{\|\nabla V\|}\right)^{-1} \int_{\Sigma_{N\bar{v}}} \frac{d\sigma}{\|\nabla V\|} F = \lim_{n \rightarrow \infty} \frac{1}{n} \sum_{i=1}^{n} F(X_i) .
\]

**Proof.** As the level sets \(\{\Sigma_{N\bar{v}}\}_{\bar{v} \in \mathbb{R}}\) are compact codimension-1 hypersurfaces of \(\mathbb{R}^N\), there exists on each of them a partition of unity \([17]\). Thus, denoting by \(\{U_i\}, 1 \leq i \leq m\), an arbitrary finite covering of \(\Sigma_{N\bar{v}}\) by means of domains of coordinates (for example by means of open balls), a set of smooth functions \(\{\varphi_i\}\) exists, with \(1 \geq \varphi_i \geq 0\) and \(\sum_i \varphi_i = 1\), for any point of \(\Sigma_{N\bar{v}}\). Since the hypersurfaces \(\Sigma_{N\bar{v}}\) are compact and oriented, the partition of the unity \(\{\varphi_i\}\) on \(\Sigma_{N\bar{v}}\), subordinate to a collection \(\{U_i\}\) of one-to-one local parametrizations
of $\Sigma_{N\theta}$, allows to represent the integral of a given smooth $(N-1)$-form $\omega$ as follows

$$\int_{\Sigma_{N\theta}} \omega^{(N-1)} = \int_{\Sigma_{N\theta}} \left( \sum_{i=1}^{m} \varphi_i(x) \right) \omega^{(N-1)}(x) = \sum_{i=1}^{m} \int_{U_i} \varphi_i \omega^{(N-1)}(x).$$

Now we proceed constructively by showing how a Monte Carlo Markov Chain (MCMC), having (27) as its probability measure, is constructed on a given $\Sigma_{N\theta}$.

We consider sequences of random values $\{x_i : i \in \Lambda\}$, with $\Lambda$ the finite set of indexes of the elements of the partition of the unity on $\Sigma_{N\theta}$, and $x_i = (x_1^i, \ldots, x_{N-1}^i)$ the local coordinates with respect to $U_i$ of an arbitrary representative point of the set $U_i$ itself. Then we define the weight $\pi(i)$ of the $i$-th element of the partition as

$$\pi(i) = \left( \sum_{k=1}^{m} \int_{U_k} \varphi_k \frac{d\sigma}{\|\nabla V\|} \right)^{-1} \int_{U_i} \varphi_i \frac{d\sigma}{\|\nabla V\|}$$

and the transition matrix elements [18]

$$p_{ij} = \min \left[ 1, \frac{\pi(j)}{\pi(i)} \right]$$

which satisfy the detailed balance equation $\pi(i)p_{ij} = \pi(j)p_{ji}$. Starting from an arbitrary element of the partition, labeled by $i_0$, and using the transition probability [28] we obtain a random Markov chain $\{i_0, i_1, \ldots, i_k, \ldots\}$ of indexes and, consequently, a random Markov chain of points $\{x_{i_0}, x_{i_1}, \ldots, x_{i_k}, \ldots\}$ on the hypersurface $\Sigma_{N\theta}$. Now, let $(x^1_P, \ldots, x^{N-1}_P)$ be the local coordinates of a point $P$ on $\Sigma_{N\theta}$ and define a local reference frame as $\{\partial/\partial x^1_P, \ldots, \partial/\partial x^{N-1}_P, n(P)\}$ where $n(P)$ is the outward unit normal vector at $P$; through the point-dependent matrix which operates the change from this basis to the canonical basis $\{e_1, \ldots, e_N\}$ of $\mathbb{R}^N$ we can associate to the Markov chain $\{x_{i_0}, x_{i_1}, \ldots, x_{i_k}, \ldots\}$ an equivalent chain $\{X_{i_0}, X_{i_1}, \ldots, X_{i_k}, \ldots\}$ of points identified through their coordinates in $\mathbb{R}^N$ but still constrained to belong to the subset $V(X) = v$, that is to $\Sigma_{N\theta}$. By construction, this Monte Carlo Markov Chain has the probability density [27] as its invariant probability measure [18], moreover, for smooth functions $F$, smooth potentials $V$ and in the absence of critical points, $F/\|\nabla V\|$ has a limited variation on each set $U_i$, thus the partition of the unity can be made as fine grained as needed – keeping it finite – to make Lebesgue integration convergent, hence Equation (28) follows. □

In part B we shall need the $N$-dependence of the momenta, up to the fourth order, of the sum of a large number $N$ of mutually independent random variables.
These $N$-dependences are worked out in what follows by using and extending some results due to Khinchin [19].

**Definition 7** Let us consider a sequence \( \{ \eta_k \}_{k=1, \ldots, N} \) of mutually independent random quantities with probability densities \( \{ u_k(x) \}_{k=1, \ldots, N} \). Let us denote with 
\[
    a_k = \int x \ u_k(x) \ dx \quad \text{the mean of the } k\text{-th quantity and with}
\]
\[
    b_k = \int (x - a_k)^2 \ u_k(x) \ dx \quad c_k = \int (x - a_k)^3 \ u_k(x) \ dx
\]
\[
    d_k = \int (x - a_k)^4 \ u_k(x) \ dx \quad e_k = \int (x - a_k)^5 \ u_k(x) \ dx
\]
its higher moments.

**Theorem 3** (Khinchin) Let us consider a sequence \( \{ \eta_k \}_{k=1, \ldots, N} \) of mutually independent random quantities with probability densities \( \{ u_k(x) \}_{k=1, \ldots, N} \). Without any significant loss of generality we assume that the \( a_k \) are zero. Under the conditions of validity of the Central Limit Theorem (see [19]), the probability density \( U_N(x) \) of 
\[
    s_N = \sum_{k=1}^{N} \eta_k
\]
is given by
\[
    U_N(x) = \frac{1}{(2\pi B_N)^{\frac{1}{2}}} \exp \left[ - \frac{x^2}{2B_N} \right] + \frac{S_N + T_Nx}{B_N^2} + O \left( \frac{1+ |x|^3}{N^2} \right), \quad \forall \ |x| < 2 \log^2 N \quad (31)
\]
\[
    U_N(x) = \frac{1}{(2\pi B_N)^{\frac{1}{2}}} \exp \left[ - \frac{x^2}{2B_N} \right] + O \left( \frac{1}{N} \right), \quad \forall x \quad (32)
\]
where \( B_N = \sum_{i=1}^{N} b_i \) and where \( S_N \) and \( T_N \) are independent of \( x \) such that \( \lim_{N \to \infty} N^{-1} S_N \) and \( \lim_{N \to \infty} N^{-1} T_N \) are finite values (allowed to vanish) and where \( \log^2 N \) stands for \( (\log N)^2 \).

**Lemma 7** Consider a sequence \( \{ \eta_k \}_{k=1, \ldots, N} \) of zero mean, mutually independent, random variables with probability densities \( \{ u_k(x) \}_{k=1, \ldots, N} \). Denote with 
\[
    B'_N, \quad C'_N \quad \text{and } D'_N \quad \text{the second, third and fourth moments respectively of } s'_N = \frac{1}{N} \sum_{k=1}^{N} \eta_k, \quad \text{and with } K'_N = D'_N - 3B'_N^2 \quad \text{the fourth cumulant of } s'_N.\]
If the random quantities fulfill the hypotheses of the Central Limit Theorem, then

\[(i) \quad \lim_{N \to \infty} N B'_N = \text{cst} < \infty \]

\[(ii) \quad \lim_{N \to \infty} N^2 C'_N = 0 \]

\[(iii) \quad \lim_{N \to \infty} N^3 K'_N = 0 \]

**Proof.**

**Assertion (i).**

Let \( \tilde{B}_N \) be the second moment of \( s_N = \sum_{k=1}^{N} \eta_k \). After Theorem 3 we have

\[
\tilde{B}_N = \int |x|^2 \tilde{U}_N(x) dx = \frac{1}{(2\pi B_N)^{\frac{1}{2}}} \int |x|^2 \exp \left(-\frac{x^2}{2B_N}\right) dx + \int |x|^2 R_N(x) dx
\]

where \( R_N(x) \) is a remainder of order \( 1/N \). The r.h.s. of this equation is the second moment of the gaussian distribution which is just \( B_N \). Then \( \tilde{B}_N \) can be rewritten, using again Theorem 3 as

\[
\lim_{N \to \infty} \tilde{B}_N = \lim_{N \to \infty} B_N + \lim_{N \to \infty} \int_{|x| < 2\log^2 N} |x|^2 \frac{S_N + T_N x}{B_N^2} dx
\]

\[
= \lim_{N \to \infty} B_N + \frac{2^4}{3} \lim_{N \to \infty} \frac{S_N \log^6 N}{B_N^2}
\]

Now let \( U'_{N}(x) \) be the probability density of \( s'_N = \frac{1}{N} \sum_{k=1}^{N} \eta_k \), its second moment \( B'_N \) is equal to

\[
B'_N = \int |x|^2 U'_{N}(x) dx = \frac{1}{N^2} \tilde{B}_N
\]

and thus

\[
\lim_{N \to \infty} N B'_N = \lim_{N \to \infty} \frac{B_N}{N} + \frac{2^4}{3} \lim_{N \to \infty} \frac{S_N \log^6 N}{N B_N^2}.
\]
Since \( \lim_{N \to \infty} N^{-1} B_N \) is a finite non-vanishing value and \( \lim_{N \to \infty} N^{-1} S_N \) is a finite value, we conclude that
\[
\lim_{N \to \infty} N B_N' = \text{cst} < \infty.
\] (35)

**Proof.** *Assertion (ii).*
Let \( \tilde{C}_N \) be the third moment of \( s_N = \sum_{k=1}^{N} \eta_k \). After Theorem 3 we have
\[
\tilde{C}_N = \int |x|^3 \tilde{U}_N(x) dx
\]
\[
= \frac{1}{(2\pi B_N)^{1/2}} \int |x|^3 \exp \left( -\frac{x^2}{2B_N} \right) dx + \int |x|^3 R_N(x) dx
\]
where \( R_N(x) \) is a remainder of order \( 1/N \). The first term of the r.h.s. is identically vanishing because it is an odd moment of a Gaussian distribution.

Thus \( \tilde{C}_N \) can be rewritten, using again Theorem 3, as
\[
\lim_{N \to \infty} \tilde{C}_N = \lim_{N \to \infty} \int_{|x| < 2 \log^2 N} |x|^3 \frac{S_N + T_N x}{B_N^{1/2}} dx
\]
\[
= 2 \left( \frac{2}{B_N} \right) \lim_{N \to \infty} \frac{S_N \log^8 N}{B_N^{3/2}}
\]
Now let \( U'_N(x) \) be the probability density of \( s'_N = \frac{1}{N} \sum_{k=1}^{N} \eta_k \), its third moment \( C'_N \) is equal to
\[
C'_N = \int |x|^3 U'_N(x) dx = \frac{1}{N^3} \tilde{C}_N
\]
which leads to the conclusion
\[
\lim_{N \to \infty} N^2 C'_N = 2^3 \lim_{N \to \infty} \frac{S_N \log^8 N}{N B_N^{3/2}} = 0.
\] (36)

**Proof.** *Assertion (iii).*
Let \( \tilde{K}_N \) be the fourth cumulant of \( s_N = \sum_{k=1}^{N} \eta_k \). we have
\[
\tilde{K}_N = \frac{1}{3} \int x^4 \tilde{U}_N(x) dx - \left( \int x^2 \tilde{U}_N(x) dx \right)^2
\] (37)
which, using Theorem 3 can be written as
\[
\tilde{K}_N = \frac{1}{3} \int x^4 G_N(x) dx - \left( \int x^2 G_N(x) dx \right)^2
\]
\[+ \frac{1}{3} \int x^4 R_N(x) dx - \left( \int x^2 R_N(x) dx \right)^2 - 2 \int x^2 R_N(x) dx \int x^2 G_N(x) dx
\]
where $G_N(x) = (2\pi B_N)^{-\frac{1}{2}} \exp \left[ -\frac{x^2}{2B_N} \right]$ is a gaussian probability distribution and $R_N(x)$ the remainder of order $1/N$.

The sum of the first two terms of the r.h.s. of the equation above is the fourth cumulant of a gaussian distribution, thus vanishing.

Again using Theorem 3 we can write

$$\lim_{N \to \infty} \tilde{K}_N = \frac{1}{3} \lim_{N \to \infty} \int_{|x| < 2 \log^2 N} x^4 \frac{S_N + T_N x}{B_N^2} dx - \left( \int_{|x| < 2 \log^2 N} x^2 \frac{S_N + T_N x}{B_N^2} dx \right)^2 - \lim_{N \to \infty} \int_{|x| < 2 \log^2 N} x^2 \frac{S_N + T_N x}{B_N^2} dx \int x^2 G_N(x) dx = \frac{2^6}{15} \lim_{N \to \infty} \frac{\log^{10} N}{N B_N^2} S_N - \frac{2^8}{9} \lim_{N \to \infty} \frac{\log^{12} N}{N B_N^2} S_N^2 - \frac{2^4}{3} \lim_{N \to \infty} \frac{\log^6 N}{N B_N^2} S_N.$$

(38)

Knowing that $\lim_{N \to \infty} N^{-1} B_N$ is a finite non-vanishing value, that $\lim_{N \to \infty} N^{-1} S_N$ is a finite value, that $\int x^2 G_N(x) dx \equiv B_N$, and that

$$K'_N = \frac{1}{3} \int |x|^4 U_N'(x) dx - \left( \int |x|^2 U_N'(x) dx \right)^2 = \frac{1}{N^4} \tilde{K}_N$$

we conclude

$$\lim_{N \to \infty} N^3 K'_N = \frac{2^6}{15} \lim_{N \to \infty} \frac{\log^{10} N}{N B_N^2} S_N - \frac{2^8}{9} \lim_{N \to \infty} \frac{\log^{12} N}{N B_N^2} S_N^2 - \frac{2^4}{3} \lim_{N \to \infty} \frac{\log^6 N}{N B_N^2} S_N = 0.$$  

This completes the proof of our Lemma.

Remark 4 If $V_N$ is a standard, confining, short-range and stable potential, at large $N$ the entropy function $S_N(\bar{v}) = \frac{1}{N} \log \Omega(N \bar{v}, N)$ is an intensive quantity, that is

$$S_{2N}(\bar{v}) \simeq S_N(\bar{v}).$$
This is the obvious consequence of the well known fact that

\[ S_N(\Lambda, \tilde{v}) = S_{N_1}(\Lambda_1, \tilde{v}) + S_{N_2}(\Lambda_2, \tilde{v}) + \mathcal{O}\left(\frac{\log N}{N}\right) \]  

(39)

which is proved in textbooks [11] and which has also the important consequence summarized in the following remark.

**Remark 5** A consequence of equation (39) is that

\[ \Omega^{1/N}(\bar{N}, N_1 + N_2, \Lambda_1 \cup \Lambda_2) = \Omega^{1/N_1}(N_1, \Lambda_1) \Omega^{1/N_2}(N_2, \Lambda_2) \theta(N), \]  

(40)

where \( \theta(N) = \mathcal{O}(N^{1/N}) \to 1 \) for \( N \to \infty \). For two identical subsystems the potential energy is equally shared among them, with vanishing relative fluctuations in the \( N \to \infty \) limit.

**Lemma 8** Let \( V_N \) be a standard, short-range, stable and confining potential function bounded below. Let \( M_{[N_0, 0]}^{[N_0, N]} \) the subset of configuration space such that \( M_{[N_0, 0]}^{[N_0, N]} = \bigcup_{v \in [\bar{v}_0, \bar{v}_1]} \Sigma_v \) where \( \Sigma_v = N \) and \( v \in \mathbb{R} \), are the \( N - 1 \)-dimensional equipotential hypersurfaces \( \Sigma_v := V_N^{-1}(v) \) of \( \mathbb{R}^N \).

If for any \( \bar{v} \in [\bar{v}_0, \bar{v}_1] \) and for any \( N \), there is no critical point of \( V_N \) on \( M_{[N_0, 0]}^{[N_0, N]} \), then there exists \( N_0 \) such that for any \( N = kN_0 + q \), \( k \geq 1 \), \( 0 \leq q < N_0 \)

\[ \min_{x \in M_{[N_0, 0]}^{[N_0, N]}} \|\nabla V_N(x)\|^2 \geq C^2kN_0 - g(k, N_0) \]

where \( C = \frac{1}{\sqrt{N_0}} \min_{x \in M_{[N_0, 0]}^{[N_0, N]}} \|\nabla V_{N_0}(x)\| \)

(41)

and where \( \lim_{k, N_0 \to \infty} \frac{g(k, N_0)}{C^2kN_0} = 0 \).

**Proof.** Let us first consider the case \( N = kN_0 \), \( k \geq 1 \).

For \( k = 1 \), the property is evident because it expresses the absence of critical points on the equipotential manifolds of dimension \( N_0 \) whose label \( \bar{v} \) belongs to the interval \([\bar{v}_0, \bar{v}_1]\), a condition which is verified by hypothesis. Notice that the existence of \( C \) is ensured by the compactness of \([\bar{v}_0, \bar{v}_1]\). \( C > 0 \) is due to the absence of critical points. For \( k \) replicas of a given system of dimension \( N_0 \) it is

\[ \|\nabla V_{kN_0}(x_1, \ldots, x_N)\|^2 = \|\nabla V_{N_0}(x_1, \ldots, x_{N_0})\|^2_{(1)} + \|\nabla V_{N_0}(x_{N_0+1}, \ldots, x_{2N_0})\|^2_{(2)} + \cdots + \|\nabla V_{N_0}(x_{(k-1)N_0+1}, \ldots, x_{kN_0})\|^2_{(k)} + \|\nabla V_{N}^{(1)}\|^2_{(1)} + \cdots + \|\nabla V_{N}^{(k)}\|^2_{(k)}, \]
Finally, after Remark 5 about configuration space decomposability, and since $M^{\times k}_{[N_0^{\bar{n}_0},N_0^{\bar{n}_1}]} \subseteq M_{[N_0^{\bar{n}_0},N_0^{\bar{n}_1}]}$, in the limit $k,N_0 \to \infty$ it is $\text{meas}(M^{\times k}_{[N_0^{\bar{n}_0},N_0^{\bar{n}_1}]}) \to \text{meas}(M_{[N_0^{\bar{n}_0},N_0^{\bar{n}_1}]}$), therefore $g(k,N_0)/C^2kN_0$ has to vanish in the same limit. □

6.2 Part B

This part is devoted to the proof of the existence of uniform upper bounds as affirmed in the Lemma 4.

We shall prove that the supremum on $N$ and on $\tilde{v} \in I_\theta$ exists of up to the fourth derivative of $S_N(\tilde{v})$. The proof of the existence of $\sup_N$ will be given by
showing that the functions considered have a finite value in the \(N \to \infty\) limit for any \(\tilde{v} \in I_\tilde{v}\). The existence of the *supremum* on \(\tilde{v}\) is then a consequence of compactness \(^1\) of the set \(I_\tilde{v}\).

### 6.2.1 Proof of \(\sup_{N,\tilde{v} \in I_\tilde{v}} |S_N(\tilde{v})| < \infty\)

This directly comes from the intensive character of \(S_N\). \(\Box\)

### 6.2.2 Proof of \(\sup_{N,\tilde{v} \in I_\tilde{v}} |\frac{\partial S_N}{\partial \tilde{v}}(\tilde{v})| < \infty\)

By definition of \(S_N\) we have

\[
\frac{\partial S_N}{\partial \tilde{v}}(\tilde{v}) = \frac{1}{N} \frac{\Omega'(v,N)}{\Omega(v,N)} \frac{dv}{d\tilde{v}} = \frac{\Omega'(v,N)}{\Omega(v,N)}
\]

where \(\Omega'(v,N)\) stands for the derivative of \(\Omega(v,N)\) with respect to the potential energy value \(v = N\tilde{v}\).

The assumptions of our Main Theorem allow the use of Theorem 2 and of the derivation formula given therein, thus

\[
\Omega'(v,N) = \int_{\Sigma_v} \|\nabla V\| A\left(\frac{1}{\|\nabla V\|}\right) \frac{d\sigma}{\|\nabla V\|},
\]

whence

\[
\frac{\partial S_N}{\partial \tilde{v}}(\tilde{v}) = \frac{\Omega'(v,N)}{\Omega(v,N)} = \langle \frac{1}{\|\nabla V\|} A(1/\|\nabla V\|) \rangle_{N,v}^{\mu_c}
\]

where \(\langle \rangle_{N,v}^{\mu_c}\) stands for the configurational microcanonical average performed on the equipotential hypersurface of level \(v\).

Let us proceed to show that this derivative is bounded by a term which is independent of \(N\).

To ease notations we define

\[
\chi \equiv \frac{1}{\|\nabla V\|}
\]

so that Eq. (45) now reads

\[
\frac{\partial S_N}{\partial \tilde{v}}(\tilde{v}) = \langle \chi A(\chi) \rangle_{N,v}^{\mu_c}.
\]

\(^1\)As at any finite \(N\) all these functions are \(C^\infty\), the *supremum* always exists for finite \(N\).
It is
\[
\frac{1}{\chi} A(\chi) = \frac{\Delta V}{\|\nabla V\|^2} - 2 \frac{\partial^i V \partial^2_{ij} V \partial^j V}{\|\nabla V\|^4}
\] (48)
and hence
\[
\left| \frac{1}{\chi} A(\chi) \right| \leq \frac{\| \Delta V \|}{\|\nabla V\|^2} + 2 \frac{\| \partial^i V \partial^2_{ij} V \partial^j V \|}{\|\nabla V\|^4},
\]
where \( \partial_i V = \partial V / \partial q^i \), \( q^i \) being the \( i \)-th coordinate of configuration space \( \mathbb{R}^N \).

By applying Lemma 8 and by choosing \( N_0 < N \) large enough
\[
\left| \frac{1}{\chi} A(\chi) \right| \leq \frac{\| \Delta V \|}{\|\nabla V\|^2} + 2 \frac{\| \partial^i V \partial^2_{ij} V \partial^j V \|}{\|\nabla V\|^4},
\]
where \( N = kN_0 + q \) (\( k \geq 1, 0 \leq q < N_0 \)), \( C = \min_{\bar{v} \in [\bar{v}_0, \bar{v}_1], x \in \Sigma_{N_0}} \| \nabla V_{N_0}(x) \| \), \( G = G(k, N_0) = [1 - g(k, N_0) / (C^2 k N_0)]^{-1} \), and where the relation \( \langle A/B \rangle = \langle A \rangle / \langle B \rangle \) has been used.

Consider now the term \( \langle \| \Delta V \| \rangle_{N,v} \), one has
\[
\langle \| \Delta V \| \rangle_{N,v} = \langle \left\| \sum_{i=1}^{N} \partial^2_{ii} V \right\| \rangle_{N,v} \leq \sum_{i=1}^{N} \langle \| \partial^2_{ii} V \| \rangle_{N,v} \leq N \max_{i=1,...,N} \langle \langle \| \partial^2_{ii} V \| \rangle \rangle_{N,v}
\]
The factorization of configuration space (Remark 5) ensures that \( \max_{i=1,...,N} \langle \| \partial^2_{ii} V \| \rangle_{N,v} \) cannot depend on \( N \), because at large \( N \) each subsystem of the total system has in the average a potential energy proportional to its size \( N_0 \).

The same reasoning holds for \( \langle \| \partial^i V \partial^2_{ij} V \partial^j V \| \rangle_{N,v} \) and \( \max_{i=1,...,N} \langle \langle \| \partial^2_{ij} V \partial^j V \| \rangle \rangle_{N,v} \).

Moreover, by denoting \( m_1 = \max_{i=1,...,N} \langle \langle \| \partial^2_{ii} V \| \rangle \rangle_{N,v} \) and
\( m_2 = \max_{i,j=1,...,N} \left( \left| \partial^2 V \partial_{ij}^2 V \partial^2 V \right| \right)_{N,v} \), by using Lemma 8 we obtain

\[
\left| \left\langle \frac{1}{\chi} A(\chi) \right\rangle_{N,v}^{\mu_c} \right| \leq \frac{m_1}{C^2} \left( 1 + \frac{q}{kN_0} \right) G + 2 \frac{n_p m_2}{C^4} \left( \frac{1}{kN_0} + \frac{q}{k^2N_0^2} \right) G^2 \tag{49}
\]

where \( n_p \) is the number of nearest neighbors, \( \lim_{N \to \infty} k = \infty \) by construction, and \( \lim_{N \to \infty} G = 1 \).

The upper bound thus obtained ensures that \( \sup_{N,v \in I} \left| \frac{\partial S_N}{\partial \bar{v}}(\bar{v}) \right| < \infty \). □

**Remark 6** Since the function \( G \) does not modify the \( N \)-dependence of the derivatives of the entropy in the limit \( N \to \infty \), for the sake of notation in what follows we shall omit \( G \).

**Remark 7** Notice that the above computations show that

\[
\lim_{N \to \infty} \left\langle \frac{A(\chi)}{\chi} \right\rangle_{N,v}^{\mu_c} = \text{const} < \infty
\]

which follows from the boundedness of \( |\langle A(\chi)/\chi \rangle| \).

### 6.2.3 Proof of \( \sup_{N,v \in I} \left| \frac{\partial^2 S_N}{\partial \bar{v}^2}(\bar{v}) \right| < \infty \)

The second derivative of \( S_N \) can be rewritten in the form

\[
\frac{\partial^2 S_N}{\partial \bar{v}^2}(\bar{v}) = N \cdot \left[ \frac{\Omega''(v,N)}{\Omega(v,N)} - \left( \frac{\Omega'(v,N)}{\Omega(v,N)} \right)^2 \right] \tag{50}
\]

or, by using the same notations as before,

\[
\frac{\partial^2 S_N}{\partial \bar{v}^2}(\bar{v}) = N \left\{ \left\langle \frac{1}{\chi} A^2(\chi) \right\rangle_{N,v}^{\mu_c} - \left( \frac{1}{\chi} A(\chi) \right)_{N,v}^{\mu_c} \right\}^2 \tag{51}
\]

again we are going to show that an upper bound, independent of \( N \), exists also for this derivative. In order to make notations compact, we define

\[
\psi \equiv \frac{\nabla}{\|\nabla V\|}
\]

for any \( h_1, h_2 \), \( \psi(h_1) \cdot \psi(h_2) = \sum_{i=1}^{N} \psi_i(h_1)\psi_i(h_2) \)
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whence simple algebra yields

\[ \psi(V) \cdot \psi(\chi) = \chi^2 M_1 - \chi^3 \Delta V, \quad (52) \]
\[ \psi^2(V) = \psi(\psi(V)) = \frac{1}{\chi} \psi(V) \cdot \psi(\chi) + \chi^2 \Delta V \quad (53) \]
\[ \psi_1(\psi_j(V)) = \chi^2 \partial^2_j V - \chi^2 \psi_j(V) \psi_k(V) \partial^2_k V \quad (54) \]
\[ \psi_1(\chi) = -\chi^3 \partial^2_j V \psi_j(V) \quad (55) \]
\[ \psi_1(\psi_j(V)) = \chi^2 \partial^2_j V - \chi^2 \psi_j(V) \psi_k(V) \partial^2_k V \quad (56) \]
\[ \psi_1(\partial^2_j V) = \chi \partial^3_{ij} V \quad (57) \]
\[ \psi_1(\partial^2_j V) = \chi \partial^3_{ij} V \quad (58) \]

where \( M_1 = \nabla(\nabla V/\|\nabla V\|) \equiv -N \cdot (\text{mean curvature of } \Sigma_\nu). \) With these notations we have

\[ A^2(\chi) = A(A(\chi)) = A(\psi(V) \cdot \psi(\chi) + \chi^3 \Delta V) \]
\[ = \frac{1}{\chi} (A(\chi))^2 + \chi \psi(V) \cdot \psi \left( \frac{A(\chi)}{\chi} \right) \quad (59) \]

and thus Eq. (51) now reads

\[ \left| \frac{\partial^2 S_N}{\partial \bar{v}^2} \right| = N \left| \left[ \frac{A(\chi)}{\chi} \right]^{\mu_c}_{N,v} - \left[ \frac{A(\chi)}{\chi} \right]^{\mu_c}_{N,v} \right|^2 \]
\[ + N \left| \left[ \psi(V) \cdot \psi \left( \frac{A(\chi)}{\chi} \right) \right]^{\mu_c}_{N,v} \right|. \quad (60) \]

By using the relations (52)-(58), the term \( \frac{1}{\chi} A(\chi) \) is rewritten as

\[ \frac{A(\chi)}{\chi} = \frac{1}{\chi} \psi(\psi(V) \chi) = \frac{2}{\chi} \psi(V) \cdot \psi(\chi) + \chi^2 \Delta V \]
\[ = 2\chi M_1 - \chi^3 \Delta V \]
\[ = \frac{\Delta V}{\|\nabla V\|^2} - 2 \frac{\partial^i V \partial^2_j V \partial^j V}{\|\nabla V\|^4}. \quad (61) \]
Now we consider the following inequalities

$$\left \langle \frac{\partial^i V \partial^2_{ij} V \partial^j V}{\| \nabla V \|^4} \right \rangle_{N,v}^{\mu c} \leq \left \langle \frac{\sum_{i,j=1}^N |\partial^i V \partial^2_{ij} V \partial^j V|}{\| \nabla V \|^4} \right \rangle_{N,v}^{\mu c}$$

$$\leq \sum_{i,j=1}^N \left \langle \frac{|\partial^i V \partial^2_{ij} V \partial^j V|}{\| \nabla V \|^4} \right \rangle_{N,v}^{\mu c}$$

$$\leq \frac{N n_p m_2}{(kN_0)^2} \leq n_p m_2 \left( \frac{1}{kN_0} + \frac{q}{k^2N_0^2} \right)$$

(62)

where \( n_p \) is the number of nearest neighbours, \( N = kN_0 + q \) \((k \geq 1, \ 0 \leq q < N_0)\) and again \( m_2 = \max_{i,j=1,...,N} \left \langle |\partial^i V \partial^2_{ij} V \partial^j V| \right \rangle_{N,v}^{\mu c} \). As \( m_2 \) keeps a finite value for \( \lim_{N \to \infty} k = \infty \), the l.h.s. of equation (62) vanishes in the \( N \to \infty \) limit.

Thus, the larger \( N \) the better the term \( \frac{1}{\chi} A(\chi) \) is approximated by \( \xi = \sum_{i=1}^N \frac{\partial^2_{ii} V}{\| \nabla V \|} = \sum_{i=1}^N \xi_i \) where \( \xi_i = \partial^2_{ii} V / \| \nabla V \| \). Here we resort to the Lemma 6 and replace the microcanonical averages by “time” averages obtained along an ergodic stochastic process. Each term \( \xi_i \), for any \( i \), can be then considered as a stochastic process on the manifold \( \Sigma_v \) with a probability density \( u_i(\xi_i) \). In presence of short range potentials, as prescribed in the hypotheses of our Main Theorem, and at large \( N \), these processes are independent.

By simply writing \( \xi = \sum_{i=1}^N \xi_i = 1/N \sum_{i=1}^N N \xi_i \), we are allowed to apply Lemma 7 which tells us that the the second moment \( B_N' \) of the distribution of \( \xi \) is such that \( \lim_{N \to \infty} N B_N' = c < \infty \).

The first term of the r.h.s. of (60) is the second moment of \( \frac{1}{\chi} A(\chi) \) multiplied by \( N \), this term, in the light of what we have just seen, remains finite in the \( N \to \infty \) limit.

Then we consider the second term of the r.h.s. of equation (60). This can be computed with simple algebra through the relations (52-58) to give

$$\bar{\psi}(V) \cdot \psi \left( \frac{A(\chi)}{\chi} \right) = 8 \chi^4 \left( \langle \bar{\psi}(V); \psi(V) \rangle \right)^2 - 4 \chi^4 \langle \bar{\psi}(V); \psi(V) \rangle \psi(V)$$

$$- 2 \chi^4 \langle \bar{\psi}(V); \psi(V) \rangle \Delta V + \chi^3 \psi_i(V) \partial^3_{ijj} V$$

$$- 2 \chi^3 \psi_i(V) \psi_j(V) \psi_k(V) \partial^3_{ijk} V$$

(63)
where

\[
\langle \psi(V) ; \psi(V) \rangle \equiv \frac{\partial_i V \partial^2_{ij} V \partial_j V}{\|\nabla V\|_2^2} \tag{64}
\]

\[
\langle \psi(V) | \psi(V) \rangle \equiv \frac{\partial_i V \partial^2_{ij} V \partial^2_{jk} V \partial_k V}{\|\nabla V\|_2^2} \tag{65}
\]

\[
\psi_i(V) \partial^3_{ijj} V \equiv \frac{\partial_i V \partial^3_{ijj} V}{\|\nabla V\|} \tag{66}
\]

\[
\psi_i(V) \psi_j(V) \psi_k(V) \partial^3_{ijk} V \equiv \frac{\partial_i V \partial_j V \partial_k V \partial^3_{ijk} V}{\|\nabla V\|_3^3}. \tag{67}
\]

The same kind of computation developed for equations (62) gives

\[
N \langle \chi^4 \langle \psi(V) ; \psi(V) \rangle^2 \rangle_{N,v}^{\mu_c} \leq \frac{N^3 n^2 m_4}{C^6(k N_0)^4} \leq \frac{M_1}{k} + O \left( \frac{1}{k^2} \right) \tag{68}
\]

\[
N \langle \chi^4 \langle \psi(V) | \psi(V) \rangle \rangle_{N,v}^{\mu_c} \leq \frac{N^2 n^2 m_5}{C^6(k N_0)^3} \leq \frac{M_5}{k} + O \left( \frac{1}{k^2} \right) \tag{69}
\]

\[
N \langle \chi^4 \langle \psi(V) ; \psi(V) \rangle \Delta V \rangle_{N,v}^{\mu_c} \leq \frac{N^3 n_2 m_6}{C^6(k N_0)^3} \leq \frac{M_6}{k} + O \left( \frac{1}{k} \right) \tag{70}
\]

\[
N \langle \chi^3 \psi_i(V) \partial^3_{ijj} V \rangle_{N,v}^{\mu_c} \leq \frac{N^2 n_2 m_7}{C^6(k N_0)^3} \leq \frac{M_7}{k} + O \left( \frac{1}{k^2} \right) \tag{71}
\]

\[
N \langle \chi^3 \psi_i(V) \psi_j(V) \psi_k(V) \partial^3_{ijk} V \rangle_{N,v}^{\mu_c} \leq \frac{N^2 n_2 m_8}{C^6(k N_0)^3} \leq \frac{M_8}{k} + O \left( \frac{1}{k^2} \right) \tag{72}
\]

where \( N = k N_0 + q \) (\( k \geq 1, 0 \leq q < N_0 \)), \( C = \min_{\bar{v} \in [\bar{v}_0, \bar{v}_1], x \in \Sigma_{N_0}^N} \|\nabla V_{N_0}(x)\| \), for any \( i, M_i \) is independent of \( N \) and \( m_i \) represent the maxima in configuration space of the generic terms appearing in the corresponding averages.

Finally, since the ensemble of terms entering equation (60) is bounded above, we have \( \sup_{N,v} \left| \frac{\partial^2 S_N}{\partial \bar{V}_v^2} (\bar{v}) \right| < \infty \). □

**Remark 8** Notice that the above computations show that

\[
\lim_{N \to \infty} N \langle \psi(V) \cdot \psi \left( \frac{A(\chi)}{\chi} \right) \rangle_{N,v}^{\mu_c} = \text{const} < \infty.
\]
6.2.4 Proof of $\sup_{N,\bar{v} \in I_e} \left| \frac{\partial^3 S_N}{\partial \bar{v}^3} (\bar{v}) \right| < \infty$

The third derivative of $S_N$ can be expressed as

$$\frac{\partial^3 S_N}{\partial \bar{v}^3} (\bar{v}) = N^2 \left\{ \frac{\Omega'''(v,N)}{\Omega(v,N)} - 3 \frac{\Omega''(v,N) \Omega'(v,N)}{\Omega(v,N)} + 2 \left( \frac{\Omega'(v,N)}{\Omega(v,N)} \right)^3 \right\}$$

or, by using Federer's operator $A$,

$$\frac{\partial^3 S_N}{\partial \bar{v}^3} (\bar{v}) = N^2 \left\{ \langle A^3(\chi) \rangle_{N,v}^{\mu c} - 3 \langle A^2(\chi) \rangle_{N,v}^{\mu c} \langle A(\chi) \rangle_{N,v}^{\mu c} + 2 \left( \langle A(\chi) \rangle_{N,v}^{\mu c} \right)^3 \right\}$$

where

$$\frac{A^3(\chi)}{\chi} = \left( \frac{A(\chi)}{\chi} \right)^3 + 3 \frac{A(\chi)}{\chi} \psi(V) \cdot \psi \left( \frac{A(\chi)}{\chi} \right)$$

$$\frac{A^2(\chi)}{\chi} = \left( \frac{A(\chi)}{\chi} \right)^2 + \psi(V) \cdot \psi \left( \frac{A(\chi)}{\chi} \right)$$

$$\frac{A(\chi)}{\chi} = 2 \frac{\psi(V) \cdot \psi}{\chi} + \frac{\Delta V}{\| \nabla V \|^2}.$$ (76)

By substituting the expressions (74)-(76) into the r.h.s. of equation (74), we get

$$\left| \frac{\partial^3 S_N}{\partial \bar{v}^3} (\bar{v}) \right| \leq N^2 \left| \langle \psi(V) \cdot \psi \left( \frac{A(\chi)}{\chi} \right) \rangle_{N,v}^{\mu c} \right|$$

$$+ 3N^2 \left| \langle \frac{A(\chi)}{\chi} \psi(V) \cdot \psi \left( \frac{A(\chi)}{\chi} \right) \rangle_{N,v}^{\mu c} \langle \frac{A(\chi)}{\chi} \rangle_{N,v}^{\mu c} \langle \psi(V) \cdot \psi \left( \frac{A(\chi)}{\chi} \right) \rangle_{N,v}^{\mu c} \right|$$

$$+ N^2 \left| \left( \left( \frac{A(\chi)}{\chi} \right) - \langle \frac{A(\chi)}{\chi} \rangle_{N,v}^{\mu c} \right)^3 \right|_{N,v}^{\mu c}. \quad (77)$$
By explicitly expanding the first term of the r.h.s. of (77) more than 30 terms are found. Nevertheless, these terms are similar or equal to those already encountered above and, consequently, their $N$-dependence can be similarly dominated as in the inequalities (68-72).

Consider now the second term of the r.h.s. of equation (77). If we put \[ A = \frac{A(\chi)}{\chi} \quad \mathcal{P} = \frac{\psi(V) \cdot \psi\left(\frac{A(\chi)}{\chi}\right)}{N,v} \]
using equations (48) and (63) we can write

\[ A = \sum_{i=1}^{N} a_i \quad \mathcal{P} = \sum_{j=1}^{N} p_j. \]

Then

\[
\langle \frac{A(\chi)}{\chi} \frac{\psi(V)}{\chi} \cdot \frac{\psi\left(\frac{A(\chi)}{\chi}\right)}{N,v} - \frac{A(\chi)}{\chi} \rangle_{N,v} \langle \psi(V) \cdot \frac{\psi\left(\frac{A(\chi)}{\chi}\right)}{N,v} \rangle_{N,v}^{\mu c} = \langle \mathcal{A}\mathcal{P} \rangle_{N,v}^{\mu c} - \langle \mathcal{A} \rangle_{N,v}^{\mu c} \langle \mathcal{P} \rangle_{N,v}^{\mu c} \]
\[
= \sum_{i,j=1}^{N} \left( \langle a_i p_j \rangle_{N,v}^{\mu c} - \langle a_i \rangle_{N,v}^{\mu c} \langle p_j \rangle_{N,v}^{\mu c} \right). \tag{78} \]

Let us consider the terms, in the last sum, for which \( i \) and \( j \) label sites which are not nearest-neighbours\(^2\). The corresponding expressions of \( a_i \) and \( p_j \) have no common coordinate variables. Thus, when computing microcanonical averages through “time” averages along the random Markov chains of Lemma 6 we take advantage of the complete decorrelation of \( a_i \) and \( p_j \) so that

\[
\text{for any } i, j \text{ s.t. } 0 \leq i, j \leq N, \quad \langle i, j \rangle \langle a_i p_j \rangle_{N,v}^{\mu c} - \langle a_i \rangle_{N,v}^{\mu c} \langle p_j \rangle_{N,v}^{\mu c} = 0
\]

(where \( \langle i, j \rangle \) stands for \( i, j \) non nearest neighbours) which simplifies equation (78) to

\[
\langle \mathcal{A}\mathcal{P} \rangle_{N,v}^{\mu c} - \langle \mathcal{A} \rangle_{N,v}^{\mu c} \langle \mathcal{P} \rangle_{N,v}^{\mu c} = \sum_{(i,j)} \left( \langle a_i p_j \rangle_{N,v}^{\mu c} - \langle a_i \rangle_{N,v}^{\mu c} \langle p_j \rangle_{N,v}^{\mu c} \right) \]
\[
\leq N n_p \max_{(i,j)} \left( \langle a_i p_j \rangle_{N,v}^{\mu c} - \langle a_i \rangle_{N,v}^{\mu c} \langle p_j \rangle_{N,v}^{\mu c} \right). \]

\(^2\)For simplicity we are here assuming that the configurational coordinates belong to a lattice, but such a restriction is not necessary. If our potential describes a fluid, replace “nearest-neighbours” with “within the interaction range”.

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Now, equations (49) and (68-72) imply
\[ \lim_{N \to \infty} N^3 \langle a_i p_j \rangle_{N,v} < \infty \]
for any \( i,j \) s.t. \( 0 \leq i,j \leq N \), \( \langle i,j \rangle \) nearest neighbours. Thus, the second term in the r.h.s. of equation (77) is bounded independently of \( N \) in the limit \( N \to \infty \).

The third term of the r.h.s. of equation (77) is smaller than the third moment of the stochastic variable \( A(\chi)/\chi \) (multiplied by \( N^2 \)). As we have already seen, we can rewrite \( A(\chi)/\chi = (1/N) \sum_{i=1}^{N} N \partial_i V/\|\nabla V\| \) to which Lemma 7 applies thus ensuring that the third moment \( C' \) of the distribution of \( A(\chi)/\chi \) is such that \( \lim_{N \to \infty} N^2 C' = 0 \).

Finally we are left with a finite upper bound of the l.h.s. of equation (77) in the \( N \to \infty \) limit.

\[ \blacksquare \]

**Remark 9** Notice that the computations above show that
\[ \lim_{N \to \infty} N^2 \left\langle \psi(V) \cdot \psi \left( \psi(V) \cdot \psi \left( \frac{A(\chi)}{\chi} \right) \right) \right\rangle_{N,v}^{\mu_c} = \text{const} < \infty . \]

### 6.2.5 Proof of \( \sup_{N,v \in I_{\ell}} \left| \frac{\partial^4 S_N}{\partial \bar{v}^4} (\bar{v}) \right| < \infty \)

The fourth derivative of \( S_N(\bar{v}) \) is given by the expression
\[
\frac{\partial^4 S_N}{\partial \bar{v}^4} (\bar{v}) = N^3 \left\{ \frac{\Omega''(v,N)}{\Omega(v,N)^2} \right\}^2 - 4 \left( \frac{\Omega''(v,N)}{\Omega(v,N)} \right)^2 - 3 \left( \frac{\Omega''(v,N)}{\Omega(v,N)} \right)^4 \]
\[
+ N^3 \left\{ \frac{12 \Omega''(v,N) \Omega'(v,N)}{(\Omega(v,N))^3} - 6 \left( \frac{\Omega'(v,N)}{\Omega(v,N)} \right)^4 \right\} \]

Again we make use of the Federer operator \( A \) to rewrite it as
\[
\frac{\partial^4 S_N}{\partial \bar{v}^4} (\bar{v}) = N^3 \left\{ \left( \frac{A^4(\chi)}{\chi} \right)_{N,v}^{\mu_c} - 4 \left( \frac{A^3(\chi)}{\chi} \right)_{N,v}^{\mu_c} \left( \frac{A(\chi)}{\chi} \right)_{N,v}^{\mu_c} \right\}
\]
where, after trivial algebra,

\[
\frac{A^4(\chi)}{\chi} = \left(\frac{A(\chi)}{\chi}\right)^4 + 6 \left(\frac{A(\chi)}{\chi}\right)^2 \psi(V) \cdot \psi\left(\frac{A(\chi)}{\chi}\right) \\
+ 3 \left(\psi(V) \cdot \psi\left(\frac{A(\chi)}{\chi}\right)\right)^2 + 4 \frac{A(\chi)}{\chi} \psi(V) \cdot \psi\left(\psi(V) \cdot \psi\left(\frac{A(\chi)}{\chi}\right)\right) \\
+ \psi(V) \cdot \psi\left[\psi(V) \cdot \psi\left(\psi(V) \cdot \psi\left(\frac{A(\chi)}{\chi}\right)\right)\right].
\]

To make the notations more compact we use

\[
A = \frac{A(\chi)}{\chi}, \quad P = \psi(V) \cdot \psi\left(\frac{A(\chi)}{\chi}\right) \\
W = \psi(V) \cdot \psi\left(\psi(V) \cdot \psi\left(\frac{A(\chi)}{\chi}\right)\right)
\]

so that, using again equations (74-75), we obtain

\[
\left|\frac{\partial^4 S_N}{\partial \bar{v}^4}(\bar{v})\right| \leq N^3 \left|\langle \psi(V) \cdot \psi(W)\rangle_{N,v}^{\mu_c}\right| \\
+ 3N^3 \left|\langle P^2\rangle_{N,v}^{\mu_c} - \left(\langle P\rangle_{N,v}^{\mu_c}\right)^2\right| \\
+ 4N^3 \left|\langle AW\rangle_{N,v}^{\mu_c} - \langle A\rangle_{N,v}^{\mu_c} \langle W\rangle_{N,v}^{\mu_c}\right| \\
+ 6N^3 \left|\left(\langle A - \langle A\rangle_{N,v}^{\mu_c}\rangle^2\right)_{N,v}^{\mu_c} - \left(\langle P - \langle P\rangle_{N,v}^{\mu_c}\rangle\right)_{N,v}^{\mu_c}\right| \\
+ N^3 \left|\left(\langle A - \langle A\rangle_{N,v}^{\mu_c}\rangle^4\right)_{N,v}^{\mu_c} - 3 \left(\langle A - \langle A\rangle_{N,v}^{\mu_c}\rangle^2\right)_{N,v}^{\mu_c}\right|^2.
\]

Consider the first term of equation (80). It is an iterative term already considered for the third derivative. This term stems from the application of the operator \(\psi(V) \cdot \psi(\cdot)\) to the term \(W\) which in its turn stems from the application of the same operator to the term \(P\). The effect of this operator is to lower the \(N\) dependence of the function upon which it is applied by a factor \(N\) (what is simply due to the factor \(1/\|\nabla V\|^2\)). Deriving with respect to \(\bar{v}\) brings about a factor \(N\) in comparison to the derivation with respect to \(v\), therefore the first term of equation (80) is of the same order of \(N^2 \langle W\rangle_{N,v}^{\mu_c}\) and consequently, according to the Remark 9, it has a finite upper bound independent of \(N\) in the limit \(N \to \infty\).
Consider now the second term of the r.h.s. of equation (80). The Remark 8 ensures that \( \lim_{N \to \infty} N \langle P \rangle_{N,v}^{\mu_c} < \infty \). Moreover, after Lemma 7
\[
\lim_{N \to \infty} N^2 \left( \langle P - \langle P \rangle_{N,v}^{\mu_c} \rangle_{N,v}^{\mu_c} \right)^2 < \infty.
\]
(81)

Consider now the third term of the r.h.s. of equation (80). The Remarks 7 and 9 entail \( \lim_{N \to \infty} \langle A \rangle_{N,v}^{\mu_c} < \infty \) and \( \lim_{N \to \infty} N^2 \langle W \rangle_{N,v}^{\mu_c} < \infty \). Thus, after Lemma 7
\[
\lim_{N \to \infty} N^\frac{3}{2} \left( \langle A - \langle A \rangle_{N,v}^{\mu_c} \rangle_{N,v}^{\mu_c} \right) < \infty
\]
\[
\lim_{N \to \infty} N^\frac{3}{2} \left( \langle W - \langle W \rangle_{N,v}^{\mu_c} \rangle_{N,v}^{\mu_c} \right) < \infty,
\]
whence
\[
\lim_{N \to \infty} N^3 \left| \langle AW \rangle_{N,v}^{\mu_c} - \langle A \rangle_{N,v}^{\mu_c} \langle W \rangle_{N,v}^{\mu_c} \right| < \infty.
\]
(82)

Consider now the fourth term of the r.h.s. of equation (80). If we write
\[
A = \frac{1}{N} \sum_{i=1}^{N} a_i \quad P = \frac{1}{N^2} \sum_{i=1}^{N} p_i
\]
with \( a_i \) and \( p_i \) terms of order 1, we have
\[
N^3 \left| \langle A - \langle A \rangle_{N,v}^{\mu_c} \rangle_{N,v}^{\mu_c} \right|^2 \left( \langle P - \langle P \rangle_{N,v}^{\mu_c} \rangle_{N,v}^{\mu_c} \right)^{\mu_c}
\]
\[
= \frac{1}{N} \sum_{i,j,k=1}^{N} \left( \langle a_i - \langle a_i \rangle_{N,v}^{\mu_c} \rangle_{N,v}^{\mu_c} \langle a_j - \langle a_j \rangle_{N,v}^{\mu_c} \rangle_{N,v}^{\mu_c} \langle p_k - \langle p_k \rangle_{N,v}^{\mu_c} \rangle_{N,v}^{\mu_c} \right)
\]
\[
= \frac{1}{N} \sum_{i,j,k} \left( \langle a_i - \langle a_i \rangle_{N,v}^{\mu_c} \rangle_{N,v}^{\mu_c} \langle a_j - \langle a_j \rangle_{N,v}^{\mu_c} \rangle_{N,v}^{\mu_c} \langle p_k - \langle p_k \rangle_{N,v}^{\mu_c} \rangle_{N,v}^{\mu_c} \right)
\]
\[
+ \frac{1}{N} \sum_{i,j,k} \left( \langle a_i - \langle a_i \rangle_{N,v}^{\mu_c} \rangle_{N,v}^{\mu_c} \langle a_j - \langle a_j \rangle_{N,v}^{\mu_c} \rangle_{N,v}^{\mu_c} \langle p_k - \langle p_k \rangle_{N,v}^{\mu_c} \rangle_{N,v}^{\mu_c} \right)
\]
where \( \langle i, j, k \rangle \) means that at least two of the three indexes refer to non nearest neighbours sites, whereas \( \langle i, j, k \rangle \) means that the three indexes are nearest neighbours. If \( i, j, k \) are such that \( \langle i, j, k \rangle \) then at least two of the three terms \( a_i, a_j \) and \( p_k \) have no common configurational variables. The microcanonical averages are again estimated according to Lemma 6 through a stochastic process on the configurational coordinates. The random processes associated with \( a_i, a_j \) and \( p_k \) are thus completely decorrelated and one has

\[
\text{for any } i, j, k, \text{ s.t. } \langle i, j, k \rangle,
\langle a_i - \langle a_i \rangle^\mu_{c_N,v} \rangle \langle a_j - \langle a_j \rangle^\mu_{c_N,v} \rangle \langle p_k - \langle p_k \rangle^\mu_{c_N,v} \rangle = 0.
\]

Now, if we consider \( i, j, k \) such that \( \langle i, j, k \rangle \), the three terms \( a_i, a_j \) and \( p_k \) are certainly correlated but we notice that there are only \( N n_p \) terms of this kind. Thus we have

\[
\frac{1}{N} \sum_{\langle i, j, k \rangle} \langle a_i - \langle a_i \rangle^\mu_{c_N,v} \rangle \langle a_j - \langle a_j \rangle^\mu_{c_N,v} \rangle \langle p_k - \langle p_k \rangle^\mu_{c_N,v} \rangle = n^2 \max_{\langle i, k \rangle} \left\{ \langle a_i - \langle a_i \rangle^\mu_{c_N,v} \rangle, \langle p_k - \langle p_k \rangle^\mu_{c_N,v} \rangle \right\}. 
\]

Since the terms \( a_i \) and \( p_k \) are of order 1, the largest term of the preceding equation is independent of \( N \), we have thus found the upper bound of the fourth term of the r.h.s. of equation (80).

Finally, the last term of the r.h.s. of equation (80) is the fourth cumulant of the stochastic variable \( A(\chi)/\chi \) (multiplied by \( N^3 \)). As already seen above, we write \( A(\chi)/\chi = 1/N \sum_{i=1}^{N} N\partial_i V/\|\nabla V\| \) so that Lemma 7 applies and ensures that the distribution of \( A(\chi)/\chi \) has a fourth cumulant \( K'_N \) such that \( \lim_{N \to \infty} N^3 K'_N = 0 \).

The ensemble of the upper bounds thus obtained yields the final desired result. □

7 Final remarks

Let us conclude with a few comments. Earlier attempts at introducing topological concepts in statistical mechanics concentrated on macroscopic low-dimensional parameter spaces. Actually this happened after Thom’s remark that the critical point shown by the van der Waals equation corresponds to the Riemann-Hugoniot catastrophe [20]. Hence some applications of the theory of singularities of differentiable maps to the study of phase transitions followed [21]. An elegant
formulation of phase transitions as due to a topological change of some abstract vector bundle of macroscopic variables was obtained by using the Atiyah-Singer index theorem \[22, 23\] and deserves special attention.

The Main Theorem, that we have proved above, makes a new kind of link between the study of phase transitions and differential topology. In fact, in the present work we deal with the high-dimensional *microscopic* configuration space of a physical system. The level sets of the microscopic interaction potential among the particles are the configuration space submanifolds that necessarily have to change their topology in correspondence with a phase transition point. The topology changes implied here are those described within the framework of Morse theory through attachment of handles \[13\].

Notice that in our approach the role of the potential \( V \) is twofold: it determines the relevant submanifolds of configuration space and it is a good Morse function on the same space. However, for example, in the case of entropy driven phase transitions occurring in hard sphere gases, the fact that the (singular) interaction potential cannot play any longer the role of Morse function does not mean that the connection between topology and phase transitions is lost, it rather means that other Morse functions are to be used. Just to give an idea of what a good Morse function could be in this case, let us think of the sum of all the pairwise euclidean distances between the hard spheres of a system: it is real valued, it has a minimum when the density is maximum, that is for close packing, meaning that this function is bounded below. The discussion of non-degeneracy is more involved and here would be out of place, let us simply remark that Morse functions are dense and degeneracy is easily removed when necessary.

The topology of configuration space submanifolds makes also a subtle link between dynamics and thermodynamics because it affects both of them, the former because it can be seen as the geodesic flow of a suitable Riemannian metric endowing configuration space \[8\], the latter because an analytic (though approximate) relation between thermodynamic entropy and Morse indexes of the critical points of configuration space submanifolds can be worked out \[9\].

Moreover, there are “exotic” kinds of transitional phenomena in statistical physics, like the glassy transition of amorphous systems to a supercooled liquid regime, or the folding transitions in polymers and proteins, which are qualitatively unified through the so-called *landscape paradigm* \[24, 25\] which is based on the idea that the relevant physics of these systems can be understood through the study of the properties of the potential energy hypersurfaces and, in particular, of their stationary points, usually called “saddles”. That this landscape paradigm naturally goes toward a link with Morse theory and topology has been hitherto overlooked. However, though at present our Main Theorem only applies
to first and second order phase transitions, the topological approach seems to have the potentiality of unifying the mathematical description of very different kinds of phase transitions.

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