Topology and Phase Transitions I. Preliminary Results

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Abstract

In this first paper, we demonstrate a theorem that establishes a first step toward proving a necessary topological condition for the occurrence of first or second order phase transitions: we prove that the topology of certain submanifolds of configuration space must necessarily change at the phase transition point. The theorem applies to 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 both the level sets $\{\Sigma_v := V_N^{-1}(v)\}_{v \in \mathbb{R}}$ of the potential function $V_N$ and the configuration space submanifolds enclosed by the $\Sigma_v$ defined by $\{M_v := V_N^{-1}((-\infty, v])\}_{v \in \mathbb{R}}$, which are labeled by the potential energy value $v$, and where $N$ is the number of degrees of freedom. The proof of the theorem proceeds by showing that, under the assumption of diffeomorphicity of the equipotential hypersurfaces $\{\Sigma_v\}_{v \in \mathbb{R}}$, as well as of the $\{M_v\}_{v \in \mathbb{R}}$, in an arbitrary interval of values for $\bar{v} = v/N$, the Helmoltz 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. This preliminary theorem is essential to prove another theorem - in paper II - which makes a stronger statement about the relevance of topology for phase transitions.

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1. INTRODUCTION

Some years ago, based on the well known fact that an Hamiltonian flow corresponds to a geodesic flow on a suitably defined Riemannian manifold, a new explanation of the origin of Hamiltonian chaos has been proposed[1, 2]. With the aid of this "geometric viewpoint", the dynamical and geometrical signatures of phase transitions have been investigated in several models[3, 4, 5, 6, 7]. Invariably, the occurrence of a phase transition is signaled by a "cuspy" pattern of some curvature property of the underlying mechanical Riemannian manifold, whereas no particular pattern is displayed in the absence of a phase transition. On the basis of an heuristic argument[3, 4], it has been conjectured that the observed geometric signatures of phase transitions could be the consequence of a change of the topology of the mechanical manifolds. After intermediate steps[8, 9], direct evidence has been given of the actual existence of topological signatures of phase transitions. These have been put in evidence through the numerical computation of the Euler characteristic (a topologic invariant) for the level sets $\{\Sigma_v\}_{v \in \mathbb{R}}$ of the potential function of a two-dimensional lattice $\varphi^4$ model[10], through the exact analytic computation of the Euler characteristic of $\{M_v = V_N^{-1}(\{-(\infty, v]\})\}_{v \in \mathbb{R}}$ submanifolds of configuration space for a mean-field $XY$ model[11] and for a $k$-trigonometric model[12].

These results have motivated the effort to make a leap forward by proving that topology changes of configuration space submanifolds (either $\Sigma_v$ or $M_v$) are necessary for the occurrence of phase transitions, at least for a class of potentials of physical relevance.

In the present paper, a result of this kind is actually proved in the form of a necessity theorem. However, one of its basic hypotheses is somewhat too restrictive – and cannot be relaxed in the present demonstration scheme – to directly use our Main Theorem as an evident rigorous support of our former topological hypothesis[13]. This notwithstanding, the Main Theorem proved in the present paper is indispensable to prove a definitely stronger result, of a broad domain of applicability, given in paper II.
In the present paper, we prove the following theorem:

**Theorem 1.** Let $V_N(q_1, \ldots, q_N) : \mathbb{R}^N \to \mathbb{R}$, be a smooth, non-singular, finite-range potential. Denote by $\Sigma_v := V_N^{-1}(v)$, $v \in \mathbb{R}$, its level sets, or equipotential hypersurfaces, in configuration space.

Then let $\bar{v} = v/N$ be the potential energy per degree of freedom.

If 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 $\{F_N(\beta)\}_{N \in \mathbb{N}}$ 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 $C^2(I_\beta)$ 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 first Theorem, given in Section 3. Now, for any given model described by a smooth, non-singular, finite-range potential, it is in general a hard task to locate all its critical points and thus to ascertain whether the theorem actually applies to it or not. Therefore we use Theorem 1 to prove - in paper II - a second theorem which, making a direct link between thermodynamic entropy and a weighed sum of the Morse indexes of the submanifolds $M_v$, provides a general and stronger result about the relevance of configuration space topology for phase transitions. We anticipate below the formulation of this second theorem:

**Theorem 2.** Let $V_N(q_1, \ldots, q_N) : \mathbb{R}^N \to \mathbb{R}$, be a smooth, non-singular, finite-range potential. Denote by $M_v := V_N^{-1}((-\infty, v])$, $v \in \mathbb{R}$, the generic submanifold of configuration space bounded by $\Sigma_v$. Let $\{q^{(i)}_v \in \mathbb{R}^N\}_{i \in [1, N(v)]}$ be the set of critical points of the potential, that is s.t. $\nabla V_N(q^{(i)}_v) = 0$, and $N(v)$ be the number of critical points up to the potential energy value $v$. Let $\Gamma(q^{(i)}_v, \epsilon_0)$ be pseudo-cylindrical neighborhoods of the critical points, and $\mu_i(M_v)$ be the Morse indexes of $M_v$, then there exist real numbers $A(N, i, \epsilon_0)$, $g$, and real smooth functions $B(N, i, v, \epsilon_0)$ such that the following equation for the micro-
canonical configurational entropy \( S_N^{(-)}(v) \) holds

\[
S_N^{(-)}(v) = \frac{1}{N} \log \left[ \int_{M_v} \bigcup_{i=1}^{N(v)} \Gamma(q^{(i)}, \varepsilon_0) \, d^N q + \sum_{i=0}^{N} A(N, i, \varepsilon_0) \, g_i \, \mu_i(M_{v-\varepsilon_0}) \right. \\
+ \left. \sum_{n=1}^{N_{\text{top}}^{(v)}+1} B(N, i(n), v - v^{(v)}(v), \varepsilon_0) \right] ,
\]

(details and definitions are given in Section 2 of paper II), and an unbound growth with \( N \) of one of the derivatives \( |\partial^k S^{(-)}(v)/\partial v^k| \), for \( k = 3, 4 \), and thus the occurrence of a first or of a second order phase transition respectively, can be entailed only by the topological term \( \sum_{i=0}^{N} A(N, i, \varepsilon_0) \, g_i \, \mu_i(M_{v-\varepsilon_0}) + \sum_{n=1}^{N_{\text{top}}^{(v)}+1} B(N, i(n), v - v^{(v)}(v), \varepsilon_0) \).

Together, these two theorems imply that for a wide class of potentials which are good Morse functions, a first or a second order phase transition can only be the consequence of a topology change of the submanifolds \( M_v \) of configuration space.

The converse is not true: topology changes are necessary but not sufficient for the occurrence of phase transitions. As we point out in Remark 12, the above mentioned works in Refs. [10] and [11, 12] provide some hints about the sufficiency conditions but rigorous results are not yet available.

The reader can get a hold of the meaning of the main result of the present paper by reading just Section 2, Section 3 and the beginning of Section 5 where a sketch of the proof of Lemma 4 is given. In Section 3 we enunciate the Main Theorem, four main Lemmas (and give the short proofs of two of them), we give the condensed proof of the Main Theorem, we enunciate a Corollary to the Main Theorem and give its proof.

Section 5, apart from the already mentioned sketch of the proof of Lemma 4 which is the core of the proof of Theorem 1, contains the most tedious and hard reading part of the paper which is necessary to prove the Main Theorem but not to understand the meaning of the Theorem itself.

A preliminary account of Theorem 1 has been given in Ref. [14].
2. BASIC DEFINITIONS

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

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

(1)

where $d\sigma$ is a surface element of $\Sigma_v := V_N^{-1}(v)$; in what follows $\Omega(v, N)$ is also called structure integral. The norm $\|\nabla V_N\|$ is defined as $\|\nabla V_N\| = [\sum_{i=1}^N (\partial q_i V_N)^2]^{1/2}$. The configurational partition function $Z_c(\beta, N)$ is defined as

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

(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, relative to $\Sigma_v$. For any $N \in \mathbb{N}$ and $\bar{v} \in \mathbb{R}$,

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

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

$$f_N(\beta) \equiv f_N(\beta; V_N) = \frac{1}{N} \log Z_c(\beta, N).$$
Configurational microcanonical entropy, relative to the volume bounded by $\Sigma_v$. For any $N \in \mathbb{N}$ and $\bar{v} \in \mathbb{R}$,

$$S_N^{(-)}(\bar{v}) \equiv S_N^{(-)}(\bar{v}; V_N) = \frac{1}{N} \log M(N\bar{v}, N)$$

where

$$M(v, N) = \int_{(\mathbb{A}^d)^{\times N}} dq_1 \ldots dq_N \Theta[V_N(q_1, \ldots, q_N) - v] = \int_0^v d\eta \int_{\Sigma_\eta} \frac{d\sigma}{\|\nabla V_N\|},$$

(3)

with $\Theta[\cdot]$ the Heaviside step function; $M(v, N)$ is the codimension-0 subset of configuration space enclosed by the equipotential hypersurface $\Sigma_v$. The representation of $M(v, N)$ given in the r.h.s. stems from the already mentioned co-area formula in [15]. Moreover, $S_N^{(-)}(\bar{v})$ is related with the configurational canonical free energy, $f_N$, for any $N \in \mathbb{N}$ and $\bar{v} \in \mathbb{R}$, through the Legendre transform [16]

$$-f_N(\beta) = \inf_{\bar{v}} \{ \beta \cdot \bar{v} - S_N^{(-)}(\bar{v}) \},$$

(4)

yielding, for any $N \in \mathbb{N}$ and $\beta \in \mathbb{R}$,

$$-f_N(\beta) = \beta \cdot \bar{v}_N - S_N^{(-)}(\bar{v}_N)$$

(5)

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

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

(6)

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

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

(7)

Finally, for a system described by a Hamiltonian function $H$ of the kind

$$H = \sum_{i=1}^N p_i^2/2 + V_N(q_1, \ldots, q_N),$$

the Helmoltz free energy is defined by

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

(8)
whence
\[ F_N(\beta; H) = -(2\beta)^{-1} \log(\pi/\beta) - f_N(\beta, V_N)/\beta \] (9)
with its thermodynamic limit \((N \to \infty \text{ and } \text{vol}(\Lambda^d)/N = \text{const})\)
\[ F_\infty(\beta) = \lim_{N \to \infty} F_N(\beta; H) . \] (10)

**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 \((N \to \infty \text{ and } \text{vol}(\Lambda^d)/N = \text{const})\) – is only piecewise analytic. In particular, if the first-order derivative of the Helmholtz 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 Helmholtz 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, fluid case).** We say that an \(N\) degrees of freedom potential \(V_N\) is a standard potential for a fluid if it is of the form
\[ V_N : \quad \mathcal{B}_N \subset \mathbb{R}^N \to \mathbb{R} 
V_N(\vec{q}) = \sum_{i \neq j=1}^n \Psi(||\vec{q}_i - \vec{q}_j||) + \sum_{i=1}^n U_\Lambda(\vec{q}_i) \] (11)
where \(\mathcal{B}_N\) is a compact subset of \(\mathbb{R}^N\), \(N = nd\), \(\Psi\) is a real valued function of one variable such that additivity holds, and where \(U_\Lambda\) is any smoothed potential barrier to confine the particles in a finite volume \(\Lambda\), that is
\[ U_\Lambda(\vec{q}) = \begin{cases} 
0 & \text{if } \vec{q} \in \Lambda' \\
+\infty & \text{if } \vec{q} \in \Lambda^c, \text{ complement in } \mathbb{R}^N \\
\mathcal{C}^\infty & \text{function for } \vec{q} \in \Lambda \setminus \Lambda' 
\end{cases} \]
where \(\Lambda' \subset \Lambda\) and \(\Lambda'\) arbitrarily close to \(\Lambda \subset \mathbb{R}^N\), closed and bounded. \(U_\Lambda\) is a confining potential in a limited spatial volume with the additional property that given two limited \(d\)-dimensional regions of space, \(\Lambda_1\) and \(\Lambda_2\), having in common a \(d-1\)-dimensional boundary, \(U_{\Lambda_1} + U_{\Lambda_2} = U_{\Lambda_1 \cup \Lambda_2}\). By additivity we mean what follows. Consider two systems \(S_1\) and \(S_2\), having \(N_1 = n_1d\) and \(N_2 = n_2d\)
degrees of freedom, occupying volumes $\Lambda_1^d$ and $\Lambda_2^d$, having potential energies $v_1$ and $v_2$, for any $(q_1, \ldots, q_{N_1}) \in (\Lambda_1^d)^{\times n_1}$ such that $V_{N_1}(q_1, \ldots, q_{N_1}) = v_1$, for any $(q_{N_1+1}, \ldots, q_{N_1+N_2}) \in (\Lambda_2^d)^{\times n_2}$ such that $V_{N_2}(q_{N_1+1}, \ldots, q_{N_1+N_2}) = v_2$, for $(q_1, \ldots, q_{N_1+N_2}) \in (\Lambda_1^d)^{\times n_1} \times (\Lambda_2^d)^{\times n_2}$ let $V_N(q_1, \ldots, q_{N_1+N_2}) = v$ be the potential energy $v$ of the compound system $S = S_1 + S_2$ which occupies the volume $\Lambda^d = \Lambda_1^d \cup \Lambda_2^d$ and contains $N = N_1 + N_2$ degrees of freedom. If

$$v(N_1 + N_2, \Lambda_1^d \cup \Lambda_2^d) = v_1(N_1, \Lambda_1^d) + v_2(N_2, \Lambda_2^d) + v'(N_1, N_2, \Lambda_1^d, \Lambda_2^d)$$

(12)

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. Moreover, at short distances $\Psi$ must be a repulsive potential so as to prevent the concentration of an arbitrary number of particles within small, finite volumes of any given size.

**Definition 4 (Standard potential, lattice case).** We say that an $N$ degrees of freedom potential $V_N$ is a standard potential for a lattice if it is of the form

$$V_N : \mathcal{B}_N \subset \mathbb{R}^N \to \mathbb{R}$$

$$V_N(q) = \sum_{\underline{i}, \underline{j} \in \mathcal{I} \subset \mathbb{N}^d} C_{\underline{i}, \underline{j}} \Psi(\|\underline{q}_{\underline{i}} - \underline{q}_{\underline{j}}\|) + \sum_{\underline{i} \in \mathcal{I} \subset \mathbb{N}^d} \Phi(\underline{q}_{\underline{i}})$$

(13)

where $\mathcal{B}_N$ is a compact subset of $\mathbb{R}^N$. Denoting by $a_1, \ldots, a_d$ the lattice spacings, if $\underline{i} \in \mathbb{N}^d$, then $(i_1 a_1, \ldots, i_d a_d) \in \Lambda^d$. We denote by $m$ the number of lattice sites in each spatial direction, by $n = m^d$ the total number of lattice sites, by $D$ the number of degrees of freedom on each site. Thus $\underline{q}_{\underline{i}} \in \mathbb{R}^D$ for any $\underline{i}$. The total number of degrees of freedom is $N = m^d D$. Having two systems made of $N = m^d D$ degrees of freedom, whose site indexes $i^{(1)}$ and $i^{(2)}$ run over $1 \leq i_1^{(1)}, \ldots, i_d^{(1)} \leq m$, and $1 \leq i_1^{(2)}, \ldots, i_d^{(2)} \leq m$, after gluing together the two systems through a common $d - 1$ dimensional boundary the new system has indexes $i$ running over, for example, $1 \leq i_1 \leq 2m$ and $1 \leq i_2, \ldots, i_d \leq m$. If

$$v(N + N, \Lambda_1^d \cup \Lambda_2^d) = v_1(N, \Lambda_1^d) + v_2(N, \Lambda_2^d) + v'(N, N, \Lambda_1^d, \Lambda_2^d)$$

(14)

where $v'$ stands for the interaction energy between the two systems and if $v'/v_1 \to 0$ and $v'/v_2 \to 0$ for $N \to \infty$ then $V_N$ is additive.
Definition 5 (Short-range potential). In defining a short-range potential, a distinction has to be made between lattice systems and fluid systems. Given a standard potential $V_N$ on a lattice, we say that it is a short-range potential if the coefficients $C_{ij}$ are such that for any $i, j \in \mathbb{I} \subset \mathbb{N}^d$, $C_{ij} = 0$ iff $|i - j| > c$, with $c$ is definitively constant for $N \to \infty$.

Given a standard potential $V_N$ 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 $|\Psi(\|q\|)| < \|q\|^{-(d+\epsilon)}$, where $d = 1, 2, 3$ is the spatial dimension.

Definition 6 (Stable potential). We say that a potential $V_N$ is stable [16] if there exists $B \geq 0$ such that

$$V_N(q_1, \ldots, q_N) \geq -NB$$

for any $N > 0$ and $(q_1, \ldots, q_N) \in (\Lambda^d)^n$, or for $\vec{q}\in \mathbb{R}^D$, $\underline{i} \in \mathbb{I} \subset \mathbb{N}^d$, $N = m^dD$, for lattices.

Definition 7 (Confining potential). With the above definitions of standard potentials $V_N$, in the fluid case the potential is said to be confining in the sense that it contains $U_\Lambda$ which constrains the particles in a finite spatial volume, and in the lattice case the potential $V_N$ contains an on-site potential such that – at finite energy – $\|\vec{q}_{\underline{i}}\|$ is constrained in compact set of values.

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

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

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

\[ S_{∞}^{(-)}(\bar{v}) = S_{∞}(\bar{v}) \quad \text{for} \quad \bar{v} \in \bigcap_{N>N_0} dom(S_{N}^{(-)}) \cap \bigcap_{N>N_0} dom(S_{N}) \]

**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 [16], chapters 3.3 and 3.4. To prove that in the thermodynamic limit the two entropies \( S_{∞}^{(-)} \) and \( S_{∞} \) are equal, we proceed from the definitions of \( S_N^{(-)} \) and of \( \beta_N(\bar{v}) \), that is

\[ S_N^{(-)}(\bar{v}) = \frac{1}{N} \log M(N\bar{v}, N) \]

and

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

noting that from the r.h.s. of Eq.(3) we obtain

\[ \frac{dM(N\bar{v}, N)}{d\bar{v}} = N\Omega(N\bar{v}, N) \] (16)

so that

\[ \beta_N(\bar{v}) = \frac{1}{NM(N\bar{v}, N)} \frac{dM(N\bar{v}, N)}{d\bar{v}} = \frac{\Omega(N\bar{v}, N)}{M(N\bar{v}, N)} \] (17)

whence

\[ \frac{1}{N} \log \Omega(\bar{v}N, N) = \frac{1}{N} \log M(\bar{v}N, N) + \frac{1}{N} \log \beta_N(\bar{v}) . \] (18)

Because of the existence of the thermodynamic limit \( \beta(\bar{v}) \) of the sequence of functions \( \beta_N(\bar{v}) \) [see Proposition 2], for any given \( \bar{v} \in \mathbb{R} \) it is

\[ \lim_{N \to \infty} \frac{1}{N} \log \beta_N(\bar{v}) = 0 \]

thus, being \( S_N(\bar{v}) = 1/N \log \Omega(\bar{v}N, N) \), in the thermodynamic limit, that is in the limit \( N \to \infty \) with \( vol(\Lambda^d)/N = \text{const} \), for any \( \bar{v} \in \mathbb{R} \) Eq.(18) implies

\[ S_{∞}(\bar{v}) = S_{∞}^{(-)}(\bar{v}) . \] (19)

\[ \square \]
Remark 2 (Equivalent definitions of entropy). In Ref. [16] it is proved that the Legendre transform relating \( S_N^{(-)}(\bar{v}) \) with \( f_N(\beta) \) still holds true in the thermodynamic limit, that is \( S_N^{(-)}(\bar{v}) \) and \( f_\infty(\beta) \) are still related by a Legendre transform (see theorem 3.4.4 at p.55 of Ref. [16]). Thus, after equation (19) also \( S(\bar{v}) \) is related with \( f_\infty(\beta) \) by the same Legendre transform.

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

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

\[
\lim_{N \to \infty} \beta_N(\bar{v}) \equiv \beta(\bar{v})), \quad \text{for } \bar{v} \in \bigcap_{N>N_0} \text{dom}(\beta_N).
\] (20)

Proof. See Ref. [16], chapter 3.4.

Henceforth, we shall use \( V \) instead of \( V_N \) if no explicit reference the \( N \)-dependence of \( V \) is necessary.

3. MAIN THEOREM

In this Section we prove the following theorem:

Theorem 1 (Necessity condition for Phase Transitions). Let \( V_N \) be a standard, smooth, confining, short-range potential bounded from below (Definitions 3, 5, 6 and 7)

\[
V_N : \quad \mathcal{B}_N \subset \mathbb{R}^N \to \mathbb{R}
\]

\[
V_N(q) = \sum_{i,j \in \mathcal{I}_N^{sd}} C_{ij} \Psi(\|q_i - q_j\|) + \sum_{i \in \mathcal{I}_N^{sd}} \Phi(q_i)
\] (21)

Let \( (\Psi, \Phi) \) be real valued one variable functions, let \( i,j \) label interacting pairs of degrees of freedom within a short-range, and let \( \{\Sigma_v\}_{v \in \mathbb{R}} \) be the family of \( N-1 \)-dimensional equipotential hypersurfaces \( \Sigma_v := V_N^{-1}(v), v \in \mathbb{R}, \) of \( \mathbb{R}^N \).
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 $\bar{v}, \bar{v}' \in I_\bar{v} = [\bar{v}_0, \bar{v}_1]$

$$\Sigma_{N\bar{v}} \text{ is } C^\infty - \text{diffeomorphic to } \Sigma_{N\bar{v}'};$$

(notation: $\Sigma_{N\bar{v}} \approx \Sigma_{N\bar{v}'}$) then the limit entropy $S(\bar{v})$ is of differentiability class $C^3(I_{\bar{v}})$, and, consequently, $\beta(\bar{v})$ belongs to $C^2(I_{\bar{v}})$, whence the limit Helmholtz free energy function $F_\infty \in C^2(I_{\bar{v}})$, where $I_{\bar{v}}$ 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 $\partial I_{\bar{v}}$.

The idea of the proof of the Theorem 1 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 $\Sigma_{v(N)}$ and $\Sigma_{v'(N)}$ with $v(N), v'(N) \in (v_0(N), v_1(N))$ are diffeomorphic for all $N$, possibly greater than some finite $N_0$, then no phase transition can occur in the (inverse) temperature interval $[\lim_{N \to \infty} \beta(\bar{v}_0(N)), \lim_{N \to \infty} \beta(\bar{v}_1(N))]$. To this purpose we have to show that, in the limit $N \to \infty$ and $\text{vol}(\Lambda^d)/N = \text{const}$, the Helmoltz free energy $F_\infty(\beta; H)$ is at least twice differentiable as a function of $\beta = 1/T$ in the interval $[\lim_{N \to \infty} \beta(\bar{v}_0(N)), \lim_{N \to \infty} \beta(\bar{v}_1(N))]$. For the standard Hamiltonian systems that we consider throughout this paper, being $F_N(\beta) = -(2\beta)^{-1}\log(\pi/\beta) - f_N(\beta)/\beta$, 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 Theorem 1 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, such that its Hessian is non-degenerate. 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. 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, 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, we know that the level sets \( f^{-1}(v) \) with \( v \in [a, c-\varepsilon] \) and arbitrary \( \varepsilon > 0 \) are diffeomorphic because in the absence of critical points in the interval \( [a, c-\varepsilon] \) for any \( v, v' \in [a, c-\varepsilon] \), with arbitrary \( \varepsilon > 0 \), \( f^{-1}(v) \) is a deformation retraction of \( f^{-1}(v') \) through the flow associated with the vector field \( X = -\nabla f / \| \nabla f \|^2 \). Now, in the neighborhood of each critical point \( x^{i,k}_c \), the existence of the Morse chart allows to represent the function \( f \) as follows

\[
    f(x) = f(x^{i,k}_c) - x_1^2 - \cdots - x_k^2 + x_{k+1}^2 + \cdots + x_n^2, \tag{22}
\]

whence the degeneracy of the quadrics, for \( v = c \), entailing that the level set \( f^{-1}(c) \) no longer qualifies as a differentiable manifold. Thus for any \( v \in [a, c-\varepsilon] \) and arbitrary \( \varepsilon > 0 \), it is

\[
    f^{-1}(v) \not\approx f^{-1}(c). \tag{23}
\]

In conclusion, 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 \( [a, b] \). \( \square \)

Lemma 2 (Smoothness of the structure integral). Let \( V_N \) be a standard, short-range, stable and confining potential function bounded below. Let

\[
\{ \Sigma_v \}_{v \in \mathbb{R}} \]

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:

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

Proof. The proof of this Lemma is given in Section \( \Box \)

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 $x \in U$, $\lim_{N \to \infty} h_N(x) = h(x)$.

If there exists $M \in \mathbb{R}$ such that for any $N \in \mathbb{N}$ and for any $a \in U$ it is $\left| \frac{dh_N}{dx}(a) \right| \leq M$, then $h$ is continuous at $a$ for any $a \in U$.

**Proof.** From the assumption that for any $N \in \mathbb{N}$ and for any $a \in U$ it is $|h'_N(a)| \leq M$, and after the fundamental theorem of calculus, the set of functions $\{h_N\}_{N \in \mathbb{N}}$ is equilipschitzian and thus uniformly equicontinuous [19]. Then, from the Ascoli theorem on equicontinuous sets of applications [19], it follows that for any $a \in U$ the closure of the set of functions $\{h_N\}_{N \in \mathbb{N}}$ is equicontinuous, and thus the limit function $h$ is continuous at $a$ for any $a \in U$.

**Lemma 4 (Uniform upper bounds).** Let $V_N$ be a standard, short-range, stable and confining potential function bounded below. Let $\{\Sigma_v\}_{v \in \mathbb{R}}$ be the family of $(N-1)$-dimensional equipotential hypersurfaces $\Sigma_v := V_N^{-1}(v), v \in \mathbb{R}$, of $\mathbb{R}^N$, if

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

then

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

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

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

$$\text{for } \bar{v} \in I_{\bar{v}}, \text{ and for any } x \in \Sigma_{N\bar{v}}, \|\nabla V_N(x)\| \geq C > 0. \quad (24)$$

Therefore, the restriction of $V_N$

$$\tilde{V}_N = V_{V_N^{-1}(I_{N\bar{v}})} : V_N^{-1}(I_{N\bar{v}}) \subset B \rightarrow \mathbb{R} \quad (25)$$
always defines a Morse function, since $V_N$ is bounded below. Notice that

$$S_N(\cdot ; V_N)_{|I_\theta} \equiv S_N(\cdot ; \tilde{V}_N)_{|I_\theta},$$  \hspace{1cm} (26)$$
in what follows we shall drop the tilde and $V_N$ will denote the above given restriction.

Now, since the condition (24) holds for the hypersurfaces $\{\Sigma_{N\bar{v}}\}_{\bar{v} \in \theta_I}$, from Lemma 2 it follows that for any $N > N_0$, $\Omega(N\bar{v}, N)$ is actually in $C^\infty(\theta_I)$, where $\theta_I = (\bar{v}_0, \bar{v}_1)$; this implies that for any $N > N_0$, also $S_N$ belongs to $C^\infty(\theta_I)$.

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 $C^3(\theta_I)$, so that we can conclude that also $S \in C^\infty(\theta_I)$.

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

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

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

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

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 $C^2(\theta_I)$. Hence we conclude that the system $S$ does not undergo neither first nor second order phase transitions in the inverse-temperature interval $\beta \in \theta_I$. \hfill \Box

**Corollary 1.** Under the same hypotheses of Theorem 1, let $\{M_v\}_{v \in \mathbb{R}}$ be the family of the $N$-dimensional subsets $M_v := V_{N-1}((\infty, v])$, $v \in \mathbb{R}$, 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 $\bar{v}, \bar{v}' \in I_\theta = [\bar{v}_0, \bar{v}_1]$ 

$$M_{\bar{v}}$$
is $C^\infty$ – diffeomorphic to $M_{\bar{v}'}$, 16
then the limit entropy \( S(-)(\vec{v}) \) is of differentiability class \( C^3(I_\beta) \), and, consequently, \( \beta(\vec{v}) = \partial S(-)/\partial \vec{v} \) belongs to \( C^2(I_\beta) \), whence the limit Helmholtz free energy function \( F_\infty \in C^2(\partial I_\beta) \), where \( \partial I_\beta \) denotes open interior of \( \beta([\vec{v}_0, \vec{v}_1]) \), so that the system described by \( V \) has neither first nor second order phase transitions in the inverse-temperature interval \( I_\beta \).

**Proof.** If for any \( \vec{v}, \vec{v}' \in I_\beta = [\vec{v}_0, \vec{v}_1] \) it is \( M_{N\vec{v}} \approx M_{N\vec{v}'} \), then after Bott’s “critical-neck theorem” \[21\], there are no critical points of \( V_N \) in the interval \([\vec{v}_0, \vec{v}_1]\). As a consequence of the absence of critical points in \([\vec{v}_0, \vec{v}_1]\), after the “non-critical neck theorem” \[17\] for any \( \vec{v}, \vec{v}' \in I_\beta = [\vec{v}_0, \vec{v}_1] \) it is \( \Sigma_{N\vec{v}} \approx \Sigma_{N\vec{v}'} \). Now Theorem \[4\] implies \( S(\vec{v}) \in C^3(I_\beta) \), so that using Proposition \[1\] we have also \( S'(-)(\vec{v}) \in C^3(I_\beta) \). Then using equation \[5\] we have \( f_\infty(\beta) \in C^2(I_\beta) \) and thus \( F_\infty \in C^2(\partial I_\beta) \), so that neither first nor second order phase transitions can occur in the inverse temperature interval \( I_\beta = (\partial S(-)/\partial \vec{v}|_{\vec{v} = \vec{v}_0}, \partial S(-)/\partial \vec{v}|_{\vec{v} = \vec{v}_1}) \).

**4. 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 \[15, 22\]:

**Theorem (Federer, Laurence).** Let \( O \subset \mathbb{R}^p \) be a bounded open set. Let \( \psi \in C^{n+1}(\overline{O}) \) be constant on each connected component of the boundary \( \partial O \) and \( g \in C^n(O) \).
By introducing $O_{t,t'} = \{ x \in O \mid t < \psi(x) < t' \}$, 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 $x \in O_{t,t'}$, $\|\nabla \psi(x)\| \geq C$, for any $k$ s.t. $0 \leq k \leq n$, for any $v \in ]t,t']$, one has
\[
\frac{d^k F}{dv^k}(v) = \int_{\{\psi=v\}} A^k g \ d\sigma^{p-1},
\] (27)
with $Ag = \nabla \left( \frac{\nabla \psi}{\|\nabla \psi\|} \right) \frac{1}{\|\nabla \psi\|}$.

By applying this Theorem to the function $\psi$ of the Lemma 5 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 1 “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 2 we have to use Lemma 5 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 Theorem 1).

5. 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 4 are proved.

The proof of Lemma 4 is the core of the proof of Theorem 1. Thus, as the proof of Lemma 4 is lengthy, in order to ease its reading we premise a summary of it.
Sketch of the proof.

In order to prove Theorem 1, we have to show that the assumption of
diffeomorphicity among the $\Sigma_{N_\bar{v}}$ for $\bar{v} \in [\bar{v}_0, \bar{v}_1]$, entails that $S_{\infty}(\bar{v})$ is three
times differentiable. After the Ascoli theorem [19], this is proved by showing
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 $\bar{v} \in [\bar{v}_0, \bar{v}_1]$

$$\sup |S_N(\bar{v})| < \infty, \quad \sup \left| \frac{\partial^k S_N}{\partial \bar{v}^k} \right| < \infty, \quad k = 1, \ldots, 4.$$ \hfill (28)

After Definition 1 for the entropy, the first four derivatives of $S_N(\bar{v})$ are

$$\partial_{\bar{v}} S_N = (1/N)(dv/d\bar{v})\Omega'/\Omega,$$

$$\partial_{\bar{v}}^2 S_N = N[\Omega''/\Omega - (\Omega'/\Omega)^2],$$

$$\partial_{\bar{v}}^3 S_N = N^2[\Omega''''/\Omega - 3\Omega''\Omega'/\Omega + 2(\Omega'/\Omega)^3],$$

$$\partial_{\bar{v}}^4 S_N = N^3[\Omega''''/\Omega - 4\Omega''''\Omega'/\Omega^2 - 3(\Omega'/\Omega)^2 + 12\Omega''''(\Omega'/\Omega)^2/\Omega^3 - 6(\Omega'/\Omega)^4],$$

where the prime indexes stand for derivations of $\Omega(v,N)$ with respect to $v = \bar{v}N$. In order to verify whether the conditions (28) 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 ab-
sence of critical points of the potential, we can use the derivation formula

$$\frac{d^k}{dv^k} \Omega(v,N) = \int_{\Sigma_v} \|\nabla V\| A^k \left( \frac{1}{\|\nabla V\|} \right) \frac{d\sigma}{\|\nabla V\|},$$ \hfill (30)

where $A^k$ stands for $k$ iterations of the operator

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

A technically crucial step to prove the Theorem is to use the above formula

(30) to compute the derivatives of $\Omega(v,N)$, in fact these are transformed into
the surface integrals of explicitly computable combinations and powers of a
few basic ingredients, like \(\|\nabla V\|\), \(\partial V/\partial q_i\), \(\partial^2 V/\partial q_i \partial q_j\), \(\partial^3 V/\partial q_i \partial q_j \partial q_k\) and so
on.

The first uniform bound in Eq.(28), \(|S_N(\vec{v})| < \infty\), is a simple consequence
of the intensivity of \(S_N(\vec{v})\).

To prove the boundedness of the first derivative of \(S_N\), we compute its
expression by means of the first of Eqs.(29) and of Eq.(30), which reads
\[
\frac{\partial S_N}{\partial \vec{v}} = \frac{1}{\Omega} \int_{\Sigma} \left[ \frac{\Delta V}{\|\nabla V\|^2} - \frac{\sum_{i,j} \partial^i V \partial^2_{ij} V \partial^j V}{\|\nabla V\|^4} \right] \frac{d\sigma}{\|\nabla V\|},
\]
with \(\partial_i V = \partial V/\partial q^i\) and \(i, j = 1, \ldots, N\), whence (with an obvious meaning of \(\langle \cdot \rangle_{\Sigma_v}\))
\[
\left| \frac{\partial S_N}{\partial \vec{v}} \right| \leq \left\langle \frac{|\Delta V|}{\|\nabla V\|^2} \right\rangle_{\Sigma_v} + 2 \left\langle \frac{\sum_{i,j} |\partial^i V \partial^2_{ij} V \partial^j V|}{\|\nabla V\|^4} \right\rangle_{\Sigma_v},
\]
the r.h.s. of this inequality – in the absence of critical points of the potential
– can be bounded from above by (see Lemma 8)
\[
\left\langle \frac{|\Delta V|}{\|\nabla V\|^2} \right\rangle_{\Sigma_v} + O\left(\frac{1}{N}\right) + 2 \left\langle \frac{\sum_{i,j=1}^N |\partial^i V \partial^2_{ij} V \partial^j V|}{\|\nabla V\|^4} \right\rangle_{\Sigma_v} + O\left(\frac{1}{N^2}\right).
\]
As we have assumed that \(V\) is smooth and bounded below, and after the
argument put forward in Remark 5 we have \(\left\langle |\Delta V| \right\rangle_{\Sigma_v} = \left\langle \sum_{i=1}^N \partial^2_{ii} V \right\rangle_{\Sigma_v} \leq N \max_i \left\langle |\partial^2_{ii} V| \right\rangle_{\Sigma_v}\) and, as we have also assumed that \(V\) is a short range
potential, the number of non-vanishing matrix elements \(\partial^2_{ij} V\) is \(N(n_p + 1)\)
where \(n_p\) is the number of neighbouring particles in the interaction range of
the potential, thus \(\left\langle |\partial^i V \partial^2_{ij} V \partial^j V| \right\rangle_{\Sigma_v} \leq N(n_p + 1) \max_{i,j} \left\langle |\partial^i V \partial^2_{ij} V \partial^j V| \right\rangle_{\Sigma_v}\).

Moreover, the following lower bounds exist for the denominators in the
inequality (33):
\[
\langle \|\nabla V\|^2 \rangle_{\Sigma_v} \geq N \min_i \langle (\partial_i V)^2 \rangle_{\Sigma_v}, \quad \text{and} \quad \langle \|\nabla V\|^4 \rangle_{\Sigma_v} \geq N^2 \min_{i,j} \langle (\partial_i V)^2 (\partial_j V)^2 \rangle_{\Sigma_v}.
\]
Finally, putting \(m = \max_{i,j} \langle |\partial^i V \partial^2_{ij} V \partial^j V| \rangle_{\Sigma_v}, c_1 = \min_i \langle (\partial_i V)^2 \rangle_{\Sigma_v}\) and
\(c_2 = \min_{i,j} \langle (\partial_i V)^2 (\partial_j V)^2 \rangle_{\Sigma_v}\), by substituting in Eq.(33) the upper bounds for
the numerators and the lower bounds for the denominators we obtain
\[
\left| \frac{\partial S_N}{\partial \bar{v}} \right| \leq \max_i \langle | \frac{\partial^2 V}{\partial u_i} | \rangle_{\Sigma_v} + O \left( \frac{1}{N} \right) + 2 \frac{n_p m}{c_2 N} + O \left( \frac{1}{N^2} \right) \tag{34}
\]
which, in the limit \( N \to \infty \), 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. But 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.\((30)\) in the expression for \( \frac{\partial^2 S_N}{\partial \bar{v}^2} \), we get
\[
\left| \frac{\partial^2 S_N}{\partial \bar{v}^2} \right| \leq N \left| \langle \alpha^2 \rangle_{\Sigma_v} - \langle \alpha \rangle_{\Sigma_v}^2 \right| + N \left| \langle \psi(V) \cdot \psi(\alpha) \rangle_{\Sigma_v} \right| \tag{35}
\]
where \( \alpha = \|\nabla V\| \cdot (1/\|\nabla V\|) \) and \( \psi = \nabla / \|\nabla V\| \). Now, it is possible to think of the scalar function \( \alpha \) as if it were a random variable, so that the first term in the r.h.s. of Eq.\((35)\) 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 \( \Sigma_v \) are smooth, closed \(( V \) is non-singular), without critical points and representable as the union of suitable subsets of \( \mathbb{R}^{N-1} \), the standard Monte Carlo method \([24]\) 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 \( \Sigma_v \), which conveniently samples the desired measure on the surface (see Lemma 6). Along such a random walk, usually called Monte Carlo Markov Chain (MCMC), \( \alpha \) 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 what we need is just knowing that in principle a suitable MCMC exists on each
\[ \Sigma_v. \] Now, the function \( \alpha \) is the integrand in square brackets in Eq. (31), where the second term vanishes at large \( N \), as is clear from Eq. (34). Therefore, at increasingly large \( N \), the approximate expression \( \alpha = \sum_{i=1}^{N} \frac{\partial_{ii}^2 V}{\| \nabla V \|^2} \) tends to become exact. \( \alpha \) 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 \( O(1) \) 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 [25], based on the Central Limit Theorem of probability theory, \( \alpha \) is a gaussian-distributed random variable; as its variance decreases linearly with \( N \), \( \lim_{N \to \infty} N |\langle \alpha^2 \rangle_{\Sigma_v} - \langle \alpha \rangle_{\Sigma_v}^2| = \text{const} < \infty \).

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

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 \( \alpha \), and whose \( N \)-dependence is known after the above mentioned theorem due to Khinchin and Lemma 7, and those terms whose \( N \)-dependence can be found by means of the same kind of estimates given above for \( \partial_v S_N \). Eventually, after a lenghty but rather mechanical work, also the third and fourth derivatives of \( S_N \) are shown to be uniformly bounded as prescribed by Eq. (28). Whence the proof of Theorem 1.

5.1. Part A

We begin by showing that on any \((N-1)\)-dimensional hypersurface \( \Sigma_{Nv} = V_N^{-1}(Nv) = \{ X \in \mathbb{R}^N \mid V_N(X) = Nv \} \) of \( \mathbb{R}^N \), we can define a homogeneous
5.1 Part A

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 $\langle \rangle^e_{N,v}$ 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 $\Sigma_{N\bar{v}} = V^{-1}(N\bar{v})$ 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

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

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

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

**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 [23]. 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 $\Sigma_{N\bar{v}}$, allows to represent the integral of a given smooth $(N-1)$-form $\omega$ as follows

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

Now we proceed constructively by showing how a Monte Carlo Markov Chain (MCMC), having (36) as its probability measure, is constructed on a given $\Sigma_{N\bar{v}}$. 

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 \( x_i = (x_i^1, \ldots, x_i^{N-1}) \) 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

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

(38)

and the transition matrix elements

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

(39)

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 (39) 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 \( (x_P^1, \ldots, x_P^{N-1}) \) be the local coordinates of a point \( P \) on \( \Sigma_{N\theta} \) and define a local reference frame as \( \{\partial/\partial x_P^1, \ldots, \partial/\partial x_P^{N-1}, n(P)\} \) 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 (36) as its invariant probability measure (36), 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 follows.

\[
\square
\]

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 \[25\].

**Definition 8.** 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 \(a_k = \int x u_k(x) \, dx\) the mean of the \(k\)-th quantity and with

\[
\begin{align*}
    b_k &= \int (x - a_k)^2 u_k(x) \, dx, \\
    c_k &= \int |x - a_k|^3 u_k(x) \, dx, \\
    d_k &= \int (x - a_k)^4 u_k(x) \, dx, \\
    e_k &= \int |x - a_k|^5 u_k(x) \, dx
\end{align*}
\]

its higher moments.

**Theorem (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 \[25\]), the probability density \(U_N(x)\) of \(s_N = \sum_{k=1}^{N} \eta_k\) is given by

\[
U_N(x) = \frac{1}{(2\pi B_N)^{\frac{1}{2}}} \exp\left[-\frac{x^2}{2B_N}\right] + \frac{S_N + T_N x}{B_N^{\frac{3}{2}}} + O\left(\frac{1}{N}\right), \quad \forall x \in \mathbb{R} \quad (41)
\]

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 \(B'_N\), \(C'_N\) and \(D'_N\) the second, third and fourth moments respectively of \(s'_N = \frac{1}{N} \sum_{k=1}^{N} \eta_k\), and with \(K'_N = D'_N - 3B'_N^2\) the fourth cumulant of \(s'_N\).
If the random quantities fulfil 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 the above reported Khinchin theorem, we have

\[
\tilde{B}_N = \int |x|^2 \tilde{U}_N(x)dx
\]

\[
= \frac{1}{(2\pi B_N)^{\frac{3}{2}}} \int |x|^2 \exp \left[ -\frac{x^2}{2B_N} \right] dx + \int |x|^2 R_N(x)dx
\]

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 Khinchin theorem, as

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

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

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

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
\[
\lim_{N \to \infty} N B'_N = \text{cst} < \infty .
\] (44)

**Proof.** Assertion (ii).

Let \( \tilde{C}_N \) be the third moment of \( s_N = \sum_{k=1}^N \eta_k \). After Khinchin theorem we have
\[
\tilde{C}_N = \int |x|^3 \tilde{U}_N(x) dx
\]
\[
= \frac{1}{(2\pi B_N)^{3/2}} \int |x|^3 \exp \left[ -\frac{x^2}{2B_N} \right] dx + \int |x|^3 R_N(x) dx
\]
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 Khinchin theorem, as
\[
\lim_{N \to \infty} \tilde{C}_N = \lim_{N \to \infty} \int_{|x|<2 \log^2 N} |x|^3 \frac{S_N + T_N x}{B_N^2} dx
\]
\[
= \lim_{N \to \infty} \int_{|x|<2 \log^2 N} |x|^3 \frac{S_N}{B_N^2} = 2^3 \lim_{N \to \infty} \frac{S_N \log^8 N}{B_N^2} \]
Now let \( U'_N(x) \) be the probability density of \( s'_N = \frac{1}{N} \sum_{k=1}^N \eta_k \), its 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
\[
\lim_{N \to \infty} N^2 C'_N = 2^3 \lim_{N \to \infty} \frac{S_N \log^8 N}{N B_N^2} = 0 .
\] (45)

**Proof.** Assertion (iii).

Let \( \tilde{K}_N \) be the fourth cumulant of \( s_N = \sum_{k=1}^N \eta_k \) we have
\[
\tilde{K}_N = \frac{1}{3} \int x^4 \tilde{U}_N(x) dx - \left( \int x^2 \tilde{U}_N(x) dx \right)^2
\] (46)
which, using Khinchin theorem, 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 Khinchin theorem we can write

\[
\lim_{N \to \infty} \tilde{K}_N = \frac{1}{3} \lim_{N \to \infty} \int_{|x| < 2 \log^2 N} x^4 \frac{S_N + T_Nx}{B_N^2} dx \\
- \lim_{N \to \infty} \left( \int_{|x| < 2 \log^2 N} x^2 \frac{S_N + T_Nx}{B_N^2} dx \right)^2 \\
- \lim_{N \to \infty} \int_{|x| < 2 \log^2 N} x^2 \frac{S_N + T_Nx}{B_N^2} dx \int x^2 G_N(x) dx \\
= \frac{2^6}{15} \lim_{N \to \infty} \frac{\log^{10} N S_N}{B_N^5} - \frac{2^8}{9} \lim_{N \to \infty} \frac{\log^{12} N S_N^2}{B_N^7} \\
- \frac{2^4}{3} \lim_{N \to \infty} \frac{\log^6 N S_N}{B_N^3} .
\]

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

\[
\lim_{N \to \infty} N^3 K'_N = \frac{2^6}{15} \lim_{N \to \infty} \frac{\log^{10} N S_N}{N B_N^5} - \frac{2^8}{9} \lim_{N \to \infty} \frac{\log^{12} N S_N^2}{N} B_N^5 \\
- \frac{2^4}{3} \lim_{N \to \infty} \frac{\log^6 N S_N}{N B_N^3} = 0 .
\]

This completes the proof of our Lemma 7. \( \square \)
Remark 3. 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

$$NS_N(\Lambda^d, \bar{v}) = N_1S_{N_1}(\Lambda^d_1, \bar{v}) + N_2S_{N_2}(\Lambda^d_2, \bar{v}) + O(\log N) \quad (48)$$

which is proved in textbooks [16] and which has also the important consequence summarized in the following remark.

Remark 4. A consequence of equation (48) is that

$$\Omega(N\bar{v}, N_1 + N_2, \Lambda^d_1 \cup \Lambda^d_2) = \Omega(N_1\bar{v}, N_1, \Lambda^d_1) \Omega(N_2\bar{v}, N_2, \Lambda^d_2) \theta(N), \quad (49)$$

where $\theta(N)$ is such that $[\theta(N)]^{1/N} = O(N^{1/N}) \to 1$ 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.

Remark 5. In the hypotheses of Theorem 1, $V$ contains only short range interactions and its functional form does not change with $N$, i.e. the functions $\Psi$ and $\Phi$ in Definitions 3 and 4 do not depend on $N$. In other words, we are tackling physically homogeneous systems, which, at any $N$, can be considered as the union of smaller and identical subsystems. At large $N$, if a system is partitioned in a number $k$ of sufficiently large subsystems, then the generalization to $k$ components of the factorization of configuration space given in Remark 4 holds. Therefore, the averages of functions of interacting variables, belonging to a given block, do not depend neither on the subsystems where they are computed (the potential functions are the same on each block after suitable relabeling of the variables), nor on the total number $N$ of degrees of freedom.

Lemma 8. Let $\{x_i\}_{i=1,...,N}$ and $\{y_i\}_{i=1,...,N}$ be two independent sets of mutually independent non negative random quantities. Define $X = \sum_{i=1}^N x_i$ and $Y =$
\[ \sum_{i=1}^{N} y_i. \] Let \( Y > 0 \) for any realisation of the random variables \( \{y_i\}_{i=1,\ldots,N} \). Let \( \langle X \rangle \), \( \langle Y \rangle \) denote the averages over an arbitrarily large number of realisations of the sets of random variables \( \{x_i\}_{i=1,\ldots,N} \) and \( \{y_i\}_{i=1,\ldots,N} \), respectively.

In the limit \( N \to \infty \), it is
\[
\left\langle \frac{X}{Y} \right\rangle = \frac{\langle X \rangle}{\langle Y \rangle}.
\]

**Proof.** After the Khinchin Theorem recalled below Definition 8 in the large \( N \) limit both \( X \) and \( Y \) are gaussian distributed random variables. Setting \( \delta X = X - \langle X \rangle \) and \( \delta(1/Y) = 1/Y - \langle 1/Y \rangle \) we have
\[
\left\langle \frac{X}{Y} \right\rangle = \langle X \rangle \left\langle \frac{1}{Y} \right\rangle + \left\langle \delta X \delta \left( \frac{1}{Y} \right) \right\rangle . \tag{50}
\]
Moreover
\[
\left\langle \delta X \delta \left( \frac{1}{Y} \right) \right\rangle \leq \left\langle \delta Z \delta \left( \frac{1}{Z} \right) \right\rangle
\]
where \( Z = X \) if \( \langle (\delta X)^2 \rangle \geq \langle (\delta(1/Y))^2 \rangle \) or \( Z = Y \) if \( \langle (\delta Y)^2 \rangle \geq \langle (\delta X)^2 \rangle \), and
\[
\left\langle \delta Z \delta \left( \frac{1}{Z} \right) \right\rangle = 1 - 2\langle Z \rangle \left\langle \frac{1}{Z} \right\rangle + \langle Z \rangle^2 \left\langle \frac{1}{Z^2} \right\rangle . \tag{51}
\]
Now, for a gaussian random variable \( Z \) such that \( \langle Z \rangle > 0 \), we have
\[
\left\langle \frac{1}{Z} \right\rangle = \frac{1}{\langle Z \rangle} \left\langle \frac{1}{1 + (Z - \langle Z \rangle)/\langle Z \rangle} \right\rangle = \frac{1}{\langle Z \rangle} \left[ 1 + \frac{\langle (Z - \langle Z \rangle)^2 \rangle}{3\langle Z \rangle^2} + \cdots \right]
\]
where all the terms with odd powers in the series expansion of \( 1/(1 + \delta Z/\langle Z \rangle) \) vanish, and the even powers terms are powers of the quadratic term which is \( O(1/N) \), thus in the limit \( N \to \infty \)
\[
\left\langle \frac{1}{Z} \right\rangle = \frac{1}{\langle Z \rangle} . \tag{52}
\]
Using Eq.(52) in Eq.(51) we get
\[
\left\langle \delta X \delta \left( \frac{1}{Y} \right) \right\rangle \leq -1 + \frac{\langle Z \rangle^2}{\langle Z^2 \rangle} = O(1/N) ,
\]
which, used in Eq.(50) together with Eq.(52), leads to the final result. \( \square \)
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 $\bar{v} \in I_{\bar{v}}$ exists of up to the fourth derivative of $S_N(\bar{v})$. 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 $\bar{v} \in I_{\bar{v}}$. The existence of the supremum on $\bar{v}$ is then a consequence of compactness of the set $I_{\bar{v}}$.

Remark 6. In what follows, the detailed proof is given for lattice potentials $V_N$, however, in the fluid case the only difference is that the number of particles, interacting with a given one, is not preassigned. For this reason, in the fluid case, the number of particles within the interaction range of any other particle has to be replaced by its average. After the end of Section 5.2.2, more comments are given on this point.

5.2.1. Proof of $\sup_{N,\bar{v} \in I_{\bar{v}}} |S_N(\bar{v})| < \infty$

This directly comes from the intensive character of $S_N$.

5.2.2. Proof of $\sup_{N,\bar{v} \in I_{\bar{v}}} \left| \frac{\partial S_N}{\partial \bar{v}}(\bar{v}) \right| < \infty$

By definition of $S_N$ we have

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

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

The assumptions of our Main Theorem allow the use of the Federer-Laurence theorem enunciated in Section 4 and of the derivation formula given therein, thus

$$\Omega'(v,N) = \int_{\Sigma_v} \|\nabla V\| A\left(\frac{1}{\|\nabla V\|}\right) \frac{d\sigma}{\|\nabla V\|}, \quad (53)$$
whence
\[
\frac{\partial S_N}{\partial \bar{v}}(\bar{v}) = \frac{\Omega'(v, N)}{\Omega(v, N)} = \langle \| \nabla V \| A(1/\| \nabla V \|) \rangle_{N,v}^{\mu c}
\] (54)

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
\[
\chi = \frac{1}{\| \nabla V \|}
\] (55)

so that Eq. (54) now reads
\[
\frac{\partial S_N}{\partial \bar{v}}(\bar{v}) = \langle \frac{1}{\chi} A(\chi) \rangle_{N,v}^{\mu c}.
\] (56)

It is
\[
\frac{1}{\chi} A(\chi) = \frac{\Delta V}{\| \nabla V \|^2} - 2 \sum_{i,j=1}^N \partial_i V \partial_{ij}^2 V \partial_j V \| \nabla V \|^4
\] (57)

and hence
\[
\left| \frac{1}{\chi} A(\chi) \right| \leq \frac{|\Delta V|}{\| \nabla V \|^2} + 2 \left| \sum_{i,j=1}^N \partial_i V \partial_{ij}^2 V \partial_j V \right| \| \nabla V \|^4,
\]

where \( \partial_i V = \partial V / \partial q^i \), \( q^i \) being the \( i \)-th coordinate of configuration space \( \mathbb{R}^N \).

In the absence of critical points of \( V \) it is \( \| \nabla V \|^2 \geq C > 0 \), thus we can apply Lemma 8, where \( Y > 0 \) is required, to find
\[
\left| \frac{\partial S_N}{\partial \bar{v}}(\bar{v}) \right| \leq \left| \frac{\Delta V}{\| \nabla V \|^2} \right| + O \left( \frac{1}{N} \right) + 2 \left| \sum_{i,j=1}^N \partial_i V \partial_{ij}^2 V \partial_j V \right| \| \nabla V \|^4 + O \left( \frac{1}{N^2} \right).
\]

Consider now the term \( \left| \Delta V \right|_{N,v}^{\mu c} \). As the potential \( V \) is assumed smooth and bounded below, one has
\[
\left| \Delta V \right|_{N,v}^{\mu c} = \left| \left( \sum_{i=1}^N \partial_i^2 V \right) \right|_{N,v}^{\mu c} \leq \sum_{i=1}^N \left| \partial_i^2 V \right|_{N,v}^{\mu c} \leq N \max_{i=1,...,N} \left| \partial_i^2 V \right|_{N,v}^{\mu c}.
\]
As a consequence of Remark 5, at large $N$ (when the fluctuations of the averages are vanishingly small) $\max_{i=1,\ldots,N} \langle | \partial^2_{ii} V | \rangle^\mu_{N,v}$ does not depend on $N$. The same holds for $\langle | \partial^i V \partial_j V \partial^i V \partial_j V | \rangle^\mu_{N,v}$ and $\max_{i=1,\ldots,N} \langle | \partial^i V \partial_j V \partial^i V \partial_j V | \rangle^\mu_{N,v}$. We set $m_1 = \max_{i=1,\ldots,N} \langle | \partial^2_{ii} V | \rangle^\mu_{N,v}$ and $m_2 = \max_{i,j=1,\ldots,N} \langle | \partial^i V \partial_j V \partial^i V \partial_j V | \rangle^\mu_{N,v}$.

Let us now consider the terms $\langle \| \nabla V \|^2 \rangle^\mu_{N,v}$ for $n = 1, 2$. One has

$$\langle \| \nabla V \|^2 \rangle^\mu_{N,v} = \sum_{i=1}^N \langle (\partial_i V)^2 \rangle^\mu_{N,v} = \sum_{i=1}^N \langle (\partial_i V)^2 \rangle^\mu_{N,v} \geq N \min_{i=1,\ldots,N} \langle (\partial_i V)^2 \rangle^\mu_{N,v},$$

$$\langle \| \nabla V \|^4 \rangle^\mu_{N,v} = \left( \sum_{i=1}^N \langle (\partial_i V)^2 \rangle^\mu_{N,v} \right)^2 = \sum_{i,j=1}^N \langle (\partial_i V)^2 (\partial_j V)^2 \rangle^\mu_{N,v} \geq N^2 \min_{i,j=1,\ldots,N} \langle (\partial_i V)^2 (\partial_j V)^2 \rangle^\mu_{N,v}.$$ 

By setting $c_1 = \min_{i=1,\ldots,N} \langle (\partial_i V)^2 \rangle^\mu_{N,v}$ and $c_2 = \min_{i,j=1,\ldots,N} \langle (\partial_i V)^2 (\partial_j V)^2 \rangle^\mu_{N,v}$ we can finally write

$$\left| \frac{1}{\chi} A(\chi) \right|^\mu_{N,v} \leq \frac{m_1}{c_1} + O\left( \frac{1}{N} \right) + 2 \frac{n_p}{c_2} \frac{m_2}{N} + O\left( \frac{1}{N^2} \right)$$

(58)

where $n_p$ is the number of nearest neighbors. It is evident that in the limit $N \to \infty$ the r.h.s. of the equation above tends to the finite constant $m_1/c_1$.

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

**Remark 7.** Notice that, in the fluid case, the computation of quantities like $\langle (\partial_i V)^2 \rangle^\mu_{N,v}$ or $\langle | \partial^2_{ii} V | \rangle^\mu_{N,v}$ involves an a-priori unknown number of neighbors of the $i$-th particle (we say that a particle is a neighbor of another one if the distance between the two particles is smaller than the interaction range of the potential). However, the requirement that $V$ is repulsive at short distance, so that clusters of an arbitrary number of particles are forbidden, guarantees that each particle has a finite average number of neighbors. Thus, averaging quantities like the above mentioned ones yields $N$-independent values.

In order to extend to the fluid case the proofs of uniform boundedness of the derivatives of the entropy (given throughout the present Section 5.2), one has to interpret $n_p$ as the average number of neighbors of a given particle.
Remark 8. 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 \(|\langle A(\chi)/\chi \rangle|\).

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

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

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

(59)

or, by using the same notations as before,

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

(60)

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

\[
\psi \equiv \nabla \rho \nabla \psi
\]

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)
\]

whence simple algebra yields

\[
\psi(V) \cdot \psi(\chi) = \chi^2 M_1 - \chi^3 \Delta V,
\]

(61)

\[
\psi^2(V) \equiv \psi(\cdot \psi(V)) = \frac{1}{\chi} \psi(V) \cdot \psi(\chi) + \chi^2 \Delta V
\]

(62)

\[
\psi_i(\psi_j(V)) = \chi^2 \partial^2_{ij} V - \chi^2 \psi_j(V) \sum_{k=1}^{N} \psi_k(V) \partial^2_{ik} V
\]

(63)

\[
\psi_i(\chi) = -\chi^3 \sum_{j=1}^{N} \partial^2_{ij} V \psi_j(V)
\]

(64)

\[
\psi_i(\psi_j(V)) = \chi^2 \partial^2_{ij} V - \chi^2 \psi_j(V) \sum_{k=1}^{N} \psi_k(V) \partial^2_{ik} V
\]

(65)

\[
\psi_i(\partial^2_{jr} V) = \chi \partial^3_{ijr} V
\]

(66)

\[
\psi_i(\partial^2_{jj} V) = \chi \partial^3_{ijj} V
\]

(67)
where $M_1 = \nabla (\nabla V / \| \nabla V \|) \equiv -N \cdot (\text{mean curvature of } \Sigma_v)$. With these notations we have

$$A^2(\chi) = A(A(\chi)) = A(\psi(V) \cdot \psi(\chi) + \chi^2 \Delta V) = \frac{1}{\chi} (A(\chi))^2 + \chi \psi(\chi) \cdot \psi \left( \frac{A(\chi)}{\chi} \right)$$

and thus Eq. (60) now reads

$$\left| \frac{\partial^2 S_N}{\partial \vec{v}^2} \right| \leq N \left| \left\langle \left[ \frac{A(\chi)}{\chi} \right]^2 \right\rangle_{N,v}^{\mu c} - \left[ \left\langle \frac{A(\chi)}{\chi} \right\rangle_{N,v}^{\mu c} \right]^2 \right| + N \left| \left\langle \psi(V) \cdot \psi \left( \frac{A(\chi)}{\chi} \right) \right\rangle_{N,v}^{\mu c} \right|.$$  (69)

By using the relations (61)-(67), the term $\frac{1}{\chi} A(\chi)$ is rewritten as

$$\frac{A(\chi)}{\chi} = \frac{1}{\chi} \psi(\psi(V) \chi) + 2 \frac{\psi'(V) \cdot \psi(\chi) + \chi^2 \Delta V}{\chi \psi(V) \cdot \psi(\chi)} = 2 \Delta M_1 - \chi^2 \Delta V$$

$$= \frac{\Delta V}{\| \nabla V \|^2} - 2 \sum_{i,j=1}^{N} \frac{\partial^2 V \partial^2 V \partial^2 V}{\| \nabla V \|^4}.$$  (70)

Now we consider the following inequalities

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

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

$$\leq \frac{N n_p m_2}{c_2 N^2} + O \left( \frac{1}{N^2} \right)$$  (71)

where $n_p$ is the number of nearest neighbours, and again

$$m_2 = \max_{i,j=1,..,N} \left| \partial^2 V \partial^2 V \partial^2 V \right|_{N,v}^{\mu c}.$$  

As $m_2$ keeps a finite value for $\lim_{N \to \infty}$, the l.h.s. of equation (71) vanishes in the $N \to \infty$ limit.

Thus, the larger $N$ the better the term $\frac{1}{\chi} A(\chi)$ is approximated by $\xi = \sum_{i=1}^{N} \partial^2 V / \| \nabla V \|^2 = \sum_{i=1}^{N} \xi_i$ where $\xi_i = \partial^2 V / \| \nabla V \|^2$. 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 $u_v(\xi)$. 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 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 (69) 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 (69). This can be computed with simple algebra through the relations (61-67) to give

$$\psi_i(V) \psi_j(V) \psi_k(V) \partial_{ijk}^3 V = \frac{\partial_i V \partial_j V \partial_k V \partial^3_{ijk} V}{\|\nabla V\|^2} \cdot \frac{\partial_i V \partial^3_{ijk} V}{\|\nabla V\|}$$

where

$$\langle \psi(V); \psi(V) \rangle \equiv \sum_{i,j,k=1}^{N} \partial_i V \partial^2_{ij} V \partial_j V \frac{\partial^3_{ijk} V}{\|\nabla V\|^2}$$

$$\langle \psi(V)|\psi(V) \rangle \equiv \sum_{i,j,k=1}^{N} \partial_i V \partial^2_{ij} V \partial^2_{jk} V \partial_k V \frac{\partial^3_{ijk} V}{\|\nabla V\|^2}$$

$$\psi_i(V) \partial_{ijk}^3 V \equiv \frac{\partial_i V \partial^3_{ijk} V}{\|\nabla V\|}$$

$$\psi_i(V) \psi_j(V) \psi_k(V) \partial_{ijk}^3 V \equiv \frac{\partial_i V \partial_j V \partial_k V \partial^3_{ijk} V}{\|\nabla V\|^3}.$$
The same kind of computation developed for equations (71) gives

\[
N \left( \chi^4 \left( \langle \psi(V) \psi(V) \rangle \right)^2 \right)_{N,v}^{\mu_c} \leq \frac{N^3 n_p^2 m_4}{c_4 N^4} + O \left( \frac{1}{N^2} \right)
\]

(77)

\[
N \left( \chi^4 \langle \psi(V) | \psi(V) \rangle \right)_{N,v}^{\mu_c} \leq \frac{N^2 n_p^2 m_5}{c_3 N^3} + O \left( \frac{1}{N^2} \right)
\]

(78)

\[
N \left( \chi^4 \langle \psi(V) | \psi(V) \rangle \triangle V \right)_{N,v}^{\mu_c} \leq \frac{N^3 n_p m_6}{c_3 N^3} + O \left( \frac{1}{N} \right)
\]

(79)

\[
N \left( \chi^3 \sum_{i,j=1}^{N} \psi_i(V) \partial_{i j j}^3 V \right)_{N,v}^{\mu_c} \leq N^2 n_p^2 m_7 + O \left( \frac{1}{N^2} \right)
\]

(80)

\[
N \left( \chi^3 \sum_{i,j,k=1}^{N} \psi_i(V) \psi_j(V) \psi_k(V) \partial_{i j k}^3 V \right)_{N,v}^{\mu_c} \leq N^2 n_p^2 m_8 + O \left( \frac{1}{N^2} \right)
\]

(81)

where, resorting again to the argument of Remark 5, we have defined the following quantities independent of \( N \)

\[
m_4 = \max_{i,j,k,l=1,N} \langle (\partial_1 V \partial_{i j}^2 V \partial_j V)(\partial_k V \partial_{k l}^2 V \partial_l V) \rangle_{N,v}^{\mu_c}
\]

\[
m_5 = \max_{i,j,k=1,N} \langle (\partial_1 V \partial_{i j}^2 V \partial_{j k}^2 V \partial_k V) \rangle_{N,v}^{\mu_c}
\]

\[
m_6 = \max_{i,j,k=1,N} \langle (\partial_1 V \partial_{i j}^2 V \partial_j V)(\partial_{k k}^2 V) \rangle_{N,v}^{\mu_c}
\]

\[
m_7 = \max_{i,j=1,N} \langle (\partial_1 V \partial_{i j}^3 V) \rangle_{N,v}^{\mu_c}
\]

\[
m_8 = \max_{i,j,k=1,N} \langle (\partial_1 V \partial_{i j} V \partial_k V)(\partial_{j k}^3 V) \rangle_{N,v}^{\mu_c}
\]

and

\[
c_3 = \min_{i_1,\ldots,i_6=1,N} \langle (\partial_1 V)^2 (\partial_{i 2} V)^2 \cdots (\partial_{i 6} V)^2 \rangle_{N,v}^{\mu_c}
\]

\[
c_4 = \min_{i_1,\ldots,i_8=1,N} \langle (\partial_1 V)^2 (\partial_{i 2} V)^2 \cdots (\partial_{i 8} V)^2 \rangle_{N,v}^{\mu_c}
\]

so that the r.h.s. of Eqs. (79) and (80) have finite limits for \( N \to \infty \), while the r.h.s. of (77), (78) and (81) vanish in the limit \( N \to \infty \).

In conclusion, since the ensemble of terms entering equation (69) is bounded above, we have \( \sup_{N,\bar{v} \in I,} \left| \frac{\partial^2 S^N}{\partial \bar{v}^2}(\bar{u}) \right| < \infty \).

\[
\text{Remark 9. Notice that the above computations show that}
\]

\[
\lim_{N \to \infty} N \left( \psi(V) \cdot \psi \left( \frac{A(\chi)}{\chi} \right) \right)_{N,v}^{\mu_c} = \text{const} < \infty.
\]
5.2 Part B

5.2.4. Proof of $\sup_{\bar{v} \in I_e} \left| \frac{\partial^3 S_N}{\partial \bar{v}^3} (\bar{v}) \right| < \infty$

The third derivative of $S_N$ can be expressed as

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

or, by using Federer’s operator $A$,

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

where

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

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

(83)

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

(84)

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

(85)

By substituting the expressions (83)-(85) into the r.h.s. of equation (83), we get

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

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

$$+ N^2 \left| \left\langle \left( \frac{A(\chi)}{\chi} \right) - \left( \frac{A(\chi)}{\chi} \right) \right\rangle_{N,v}^{\mu_c} \right|.$$  

(86)

By explicitly expanding the first term of the r.h.s. of (86) 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 (77, 81).

Consider now the second term of the r.h.s. of equation (86). If we put

$$A = \frac{A(\chi)}{\chi} \quad \text{and} \quad \mathcal{P} = \psi(V) \cdot \psi\left(\frac{A(\chi)}{\chi}\right)$$

using equations (57) and (72) we can write

$$A = \sum_{i=1}^{N} a_i \quad \text{and} \quad \mathcal{P} = \sum_{j=1}^{N} p_j.$$

Then

$$\left\langle \frac{A(\chi)}{\chi} \psi(V) \cdot \psi\left(\frac{A(\chi)}{\chi}\right) \right\rangle_{N,v}^{\mu_c} - \left\langle \frac{A(\chi)}{\chi} \right\rangle_{N,v}^{\mu_c} \left\langle \psi(V) \cdot \psi\left(\frac{A(\chi)}{\chi}\right) \right\rangle_{N,v}^{\mu_c}$$

$$= \left\langle \mathcal{A} \mathcal{P} \right\rangle_{N,v}^{\mu_c} - \left\langle A \right\rangle_{N,v}^{\mu_c} \left\langle \mathcal{P} \right\rangle_{N,v}^{\mu_c}$$

$$= \sum_{i,j=1}^{N} \left( \langle a_i p_j \rangle_{N,v}^{\mu_c} - \langle a_i \rangle_{N,v}^{\mu_c} \langle p_j \rangle_{N,v}^{\mu_c} \right). \quad (87)$$

Let us consider the terms, in the last sum, for which $i$ and $j$ label sites which are not nearest-neighbours[27]. 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

for any $i, j$ s.t. $0 \leq i, j \leq N, \; \langle i, j \rangle$ then

$$\langle a_i p_j \rangle_{N,v}^{\mu_c} - \langle a_i \rangle_{N,v}^{\mu_c} \langle p_j \rangle_{N,v}^{\mu_c} = 0$$

(where $\langle i, j \rangle$ stands for $i, j$ non nearest neighbours) which simplifies equation (87) to

$$\left\langle \mathcal{A} \mathcal{P} \right\rangle_{N,v}^{\mu_c} - \left\langle A \right\rangle_{N,v}^{\mu_c} \left\langle \mathcal{P} \right\rangle_{N,v}^{\mu_c} = \sum_{\langle i, j \rangle} \left( \langle a_i p_j \rangle_{N,v}^{\mu_c} - \langle a_i \rangle_{N,v}^{\mu_c} \langle p_j \rangle_{N,v}^{\mu_c} \right)$$

$$\leq N n_p \max_{\langle i, j \rangle} \left( \langle a_i p_j \rangle_{N,v}^{\mu_c} - \langle a_i \rangle_{N,v}^{\mu_c} \langle p_j \rangle_{N,v}^{\mu_c} \right).$$

Now, equations (58) and (77, 81) imply

for any $i, j$ s.t. $0 \leq i, j \leq N, \; \langle i, j \rangle$ \quad $\lim_{N \to \infty} N^3 \langle a_i p_j \rangle_{N,v}^{\mu_c} < \infty$

while equations (57) and (72) imply

for any $i, j$ s.t. $0 \leq i, j \leq N, \; \langle i, j \rangle$ \quad $\lim_{N \to \infty} N^3 \langle a_i \rangle_{N,v}^{\mu_c} \langle p_j \rangle_{N,v}^{\mu_c} < \infty$, 
where \( \langle i,j \rangle \) stands for \( i,j \) nearest neighbours. Thus, the second term in the r.h.s. of equation (86) is bounded independently of \( N \) in the limit \( N \to \infty \).

The third term of the r.h.s. of equation (86) 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 \( A(\chi)/\chi = (1/N) \sum_{i=1}^{N} N \partial_{i}^{2} V / \| \nabla V \|^{2} \) to which Lemma 7 applies thus ensuring that the third moment \( C'_N \) of the distribution of \( A(\chi)/\chi \) is such that \( \lim_{N \to \infty} N^{2} C'_N = 0 \).

Finally we are left with a finite upper bound of the l.h.s. of equation (86) in the \( N \to \infty \) limit.

**Remark 10.** Notice that the computations above show that

\[
\lim_{N \to \infty} N^{2} \left( \psi(V) \cdot \psi \left( \frac{A(\chi)}{\chi} \right) \right)^{\mu_{c}}_{N,v} = \text{const} < \infty.
\]

### 5.2.5. Proof of \( \sup_{N,\tilde{v} \in I_{\tilde{v}}} \left| \frac{\partial^{4} S_{N}}{\partial \tilde{v}^{4}}(\tilde{v}) \right| < \infty \)

The fourth derivative of \( S_{N}(\tilde{v}) \) is given by the expression

\[
\frac{\partial^{4} S_{N}}{\partial \tilde{v}^{4}}(\tilde{v}) = N^{3} \left\{ \frac{\Omega^{iv}(v,N)}{\Omega(v,N)} - 4 \frac{\Omega''(v,N)}{(\Omega(v,N))^{2}} \frac{\Omega'(v,N)}{\Omega(v,N)} \right\}^{2} - 3 \left( \frac{\Omega''(v,N)}{\Omega(v,N)} \right)^{2}
\]

\[
+ \quad N^{3} \left\{ 12 \frac{\Omega''(v,N)}{(\Omega(v,N))^{3}} - 6 \left( \frac{\Omega'(v,N)}{\Omega(v,N)} \right)^{4} \right\}
\]

Again we make use of the Federer operator \( A \) to rewrite it as

\[
\frac{\partial^{4} S_{N}}{\partial \tilde{v}^{4}}(\tilde{v}) = N^{3} \left\{ \left\langle \frac{A^4(\chi)}{\chi} \right\rangle_{N,v}^{\mu_{c}} - 4 \left\langle \frac{A^3(\chi)}{\chi} \right\rangle_{N,v}^{\mu_{c}} \left\langle \frac{A(\chi)}{\chi} \right\rangle_{N,v}^{\mu_{c}} \right\}
\]

\[
- N^{3} \left\{ 3 \left\langle \frac{A^2(\chi)}{\chi} \right\rangle_{N,v}^{\mu_{c}} \right\}^{2} - 12 \left\langle \frac{A^2(\chi)}{\chi} \right\rangle_{N,v}^{\mu_{c}} \left\langle \frac{A(\chi)}{\chi} \right\rangle_{N,v}^{\mu_{c}} \right\}^{2}
\]

\[
- 6N^{3} \left( \left\langle \frac{A(\chi)}{\chi} \right\rangle_{N,v}^{\mu_{c}} \right)^{4}
\]
where, after trivial algebra,

\[
\frac{A^4(\chi)}{\chi} = \left(\frac{A(\chi)}{\chi}\right)^4 + 6 \left(\frac{A(\chi)}{\chi}\right)^2 \psi(V) \cdot \psi\left(\frac{A(\chi)}{\chi}\right)
+ 3 \left(\psi(V) \cdot \psi\left(\frac{A(\chi)}{\chi}\right)\right)^2 + 4 \frac{A(\chi)}{\chi} \psi(V) \cdot \psi\left(\psi(V) \cdot \psi\left(\frac{A(\chi)}{\chi}\right)\right)
+ \psi(V) \cdot \psi\left[\psi(V) \cdot \psi\left(\psi(V) \cdot \psi\left(\frac{A(\chi)}{\chi}\right)\right)\right].
\] (88)

To make the notations more compact we use

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

so that, using again equations (83-84), we obtain

\[
\left|\frac{\partial^4 S_N}{\partial \tilde{v}^4}(\tilde{v})\right| \leq N^3 \left|\langle \psi(V) \cdot \psi(\mathcal{W})\rangle^\mu_c\right|
+ 3N^3 \left|\langle \mathcal{P}^2\rangle^\mu_c - \left(\langle \mathcal{P}\rangle^\mu_c\right)^2\right|
+ 4N^3 \left|\langle \mathcal{A}\mathcal{W}\rangle^\mu_c - \langle \mathcal{A}\rangle^\mu_c \langle \mathcal{W}\rangle^\mu_c\right|
+ 6N^3 \left|\left(\langle \mathcal{A} - \langle \mathcal{A}\rangle^\mu_c\rangle^\mu_c \right)^2 \left(\mathcal{P} - \langle \mathcal{P}\rangle^\mu_c\right)\right|_{N,v}
+ N^3 \left|\left(\langle \mathcal{A} - \langle \mathcal{A}\rangle^\mu_c\rangle^\mu_c \right)^4\right|_{N,v}
\] (89)

Consider the first term of equation (89). 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 \(\mathcal{W}\) which in its turn stems from the application of the same operator to the term \(\mathcal{P}\). 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 \(\tilde{v}\) brings about a factor \(N\) in comparison to the derivation with respect to \(v\), therefore the first term of equation (89) is of the same order of \(N^2 \langle \mathcal{W}\rangle^\mu_c\) and consequently, according to the Remark, 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 (89). The Remark 9 ensures that \( \lim_{N \to \infty} N \langle P \rangle_{N,v}^{\mu_c} < \infty \). Moreover, after Lemma 7
\[
\lim_{N \to \infty} N^3 \left( \langle P - \langle P \rangle_{N,v}^{\mu_c} \rangle_{N,v}^{\mu_c} \right)^2 < \infty .
\]
(90)

Consider now the third term of the r.h.s. of equation (89). The Remarks 8 and 10 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
\[
\lim_{N \to \infty} N^{\frac{3}{2}} \left( \langle A - \langle A \rangle_{N,v}^{\mu_c} \rangle_{N,v}^{\mu_c} \right) < \infty
\]
\[
\lim_{N \to \infty} N^{\frac{5}{2}} \left( \langle W - \langle W \rangle_{N,v}^{\mu_c} \rangle_{N,v}^{\mu_c} \right) < \infty ,
\]
whence
\[
\lim_{N \to \infty} N^3 \left| \langle AW \rangle_{N,v}^{\mu_c} - \langle A \rangle_{N,v}^{\mu_c} \langle W \rangle_{N,v}^{\mu_c} \right| < \infty .
\]
(91)

Consider now the fourth term of the r.h.s. of equation (89). 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
\[
N^3 \left| \left( \langle A - \langle A \rangle_{N,v}^{\mu_c} \rangle_{N,v}^{\mu_c} \right)^2 \left( \langle P - \langle P \rangle_{N,v}^{\mu_c} \rangle_{N,v}^{\mu_c} \right) \right|_{N,v}^{\mu_c}
\]
\[
= \frac{1}{N} \sum_{i,j,k=1}^{N} \left( a_i - \langle a_i \rangle_{N,v}^{\mu_c} \right) \left( a_j - \langle a_j \rangle_{N,v}^{\mu_c} \right) \left( p_k - \langle p_k \rangle_{N,v}^{\mu_c} \right)_{N,v}^{\mu_c}
\]
\[
= \frac{1}{N} \sum_{i,j,k} \left( a_i - \langle a_i \rangle_{N,v}^{\mu_c} \right) \left( a_j - \langle a_j \rangle_{N,v}^{\mu_c} \right) \left( p_k - \langle p_k \rangle_{N,v}^{\mu_c} \right)_{N,v}^{\mu_c}
\]
\[
+ \frac{1}{N} \sum_{(i,j,k)} \left( a_i - \langle a_i \rangle_{N,v}^{\mu_c} \right) \left( a_j - \langle a_j \rangle_{N,v}^{\mu_c} \right) \left( p_k - \langle p_k \rangle_{N,v}^{\mu_c} \right)_{N,v}^{\mu_c}
\]
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

$$\left\langle \left( a_i - \langle a_i \rangle_{N,v}^{\mu c} \right) \left( a_j - \langle a_j \rangle_{N,v}^{\mu c} \right) \left( p_k - \langle p_k \rangle_{N,v}^{\mu c} \right) \right\rangle_{N,v}^{\mu c} = 0.$$ 

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 $N n_2^p$ terms of this kind. Thus we have

$$\frac{1}{N} \sum_{\langle i, j, k \rangle} \left\langle \left( a_i - \langle a_i \rangle_{N,v}^{\mu c} \right) \left( a_j - \langle a_j \rangle_{N,v}^{\mu c} \right) \left( p_k - \langle p_k \rangle_{N,v}^{\mu c} \right) \right\rangle_{N,v}^{\mu c} \leq n_2^p \max_{\langle i, k \rangle} \left\{ \left( a_i - \langle a_i \rangle_{N,v}^{\mu c} \right), \left( p_k - \langle p_k \rangle_{N,v}^{\mu c} \right) \right\}.$$

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 (89).

Finally, the last term of the r.h.s. of equation (89) is the fourth cumulant of the stochastic variable $A(\chi)/\chi$ (multiplied by $N^3$). As already seen above, we write $A(\chi)/\chi = 1/N \sum_{i=1}^{N} N \partial_{ii}^2 V/\|\nabla V\|^2$ 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.

6. FINAL REMARKS

To conclude this first paper, some comments are in order.

Remark 11 (Domain of physical applications). Notice that the requirement of standard, stable, confining and short-range potentials $V_N$ applies to a
broad class of physically relevant models. In fact, the interatomic and inter-
molecular 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 12 (Sufficiency conditions).** Notice that the converse of our Main
Theorem is not true, in other words there is not a one-to-one correspon-
dence between any topology change of the energy level sets and phase tran-
sitions. In fact, there are systems, like the Fermi-Pasta-Ulam model described
by $V_N(q) = \sum_{i=1}^{N} \frac{1}{2}(q_{i+1} - q_i)^2 + \frac{\lambda}{4}(q_{i+1} - q_i)^4$ which, for fixed end points, has no
critical points and no phase transitions, whereas, for example, a one dimen-
sional lattice of classical spins (or of coupled rotators) described by the potential
function $V_N(q) = \sum_{i=1}^{N} [1 - \cos(q_{i+1} - q_i)]$ has many critical points [11] so that
both families $\{\Sigma_v\}_{v \in \mathbb{R}}$ and $\{M_v\}_{v \in \mathbb{R}}$ undergo many topology changes, but, since
no phase transition is associated with this potential, none of these topology
changes corresponds to a phase transition. Note that this is not a counter ex-
ample of our Main Theorem (which would require to find a system undergoing
a phase transition in the absence of topology changes and within the domain
of validity of the Theorem), it just tells us that the loss of diffeomorphicity of
the $\{\Sigma_v\}_{v \in \mathbb{R}}$ and, equivalently, of the $\{M_v\}_{v \in \mathbb{R}}$ at some $v_c$, is a necessary but
not sufficient condition for the occurrence of a phase transition.

**Remark 13 (Relevance of topology changes for phase transitions).**
In order to prove that our Theorem is relevant to statistical mechanics, and
in particular in order to really link the phenomenon of phase transitions to
a topology change of the configuration space submanifolds $M_v$, in paper II we
work out an analytic relation between configurational entropy $S(v)$ and the
Morse indexes of the submanifolds $M_v$. Such a relation is formulated within
another Theorem (enunciated also in the Introduction of the present paper)
which unveils why the differentiability class of $S(v)$, in the $N \to \infty$ limit, can
be lowered from $C^\infty$ to $C^2$ or to $C^1$ only by a suitable energy change of the
Morse indexes (hence of topology change). Loosely speaking, in the context of
our topological approach, the Theorem proved in paper II plays an analogous role to that played by the Lee-Yang circle Theorem [28] within the context of the Yang-Lee theory of phase transitions.

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[26] As at any finite $N$ all these functions are $C^\infty$, the supremum always exists for finite $N$.

[27] 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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