



**HAL**  
open science

# Ensemble Dependence of Fluctuations: Canonical Microcanonical Equivalence of Ensembles

Nicoletta Cancrini, Stefano Olla

► **To cite this version:**

Nicoletta Cancrini, Stefano Olla. Ensemble Dependence of Fluctuations: Canonical Microcanonical Equivalence of Ensembles. *Journal of Statistical Physics*, 2017, 168 (4), pp.707 - 730. 10.1007/s10955-017-1830-y . hal-01447021v2

**HAL Id: hal-01447021**

**<https://hal.science/hal-01447021v2>**

Submitted on 27 Aug 2017

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

# ENSEMBLE DEPENDENCE OF FLUCTUATIONS. CANONICAL MICROCANONICAL EQUIVALENCE OF ENSEMBLES.

NICOLETTA CANCRINI AND STEFANO OLLA

ABSTRACT. We study the equivalence of microcanonical and canonical ensembles in continuous systems, in the sense of the convergence of the corresponding Gibbs measures and the first order corrections. We are particularly interested in *extensive* observables, like the total kinetic energy. This result is obtained by proving an Edgeworth expansion for the local central limit theorem for the energy in the canonical measure, and a corresponding local large deviations expansion. As an application we prove a formula due to Lebowitz-Percus-Verlet that express the asymptotic microcanonical variance of the kinetic energy in terms of the heat capacity.

## 1. INTRODUCTION

The relation between averages of observables of a physical system with respect to different phase-space ensembles permits to prove what is called the *equivalence of ensembles*. That is, in the thermodynamic limit (size of the system goes to  $\infty$ ), the probability distribution of a local observable is independent of the ensemble used. Whether the microcanonical and the canonical ensembles give the same physical predictions was studied from the beginning of statistical mechanics, starting from Boltzmann introduction of distributions on phase space [1] and Gibbs formulation of the ensembles in their modern probabilistic form [2],

There are many different aspects and approaches to determine if the different ensembles give the same predictions. The idea to apply local limit theorems to the problem of equivalence of ensembles goes back to the book of Khinchin [10]. The equivalence between canonical and grandcanonical ensembles, using the central limit theorem, was proved in the seminal article of Dobrushin and Tirozzi [7] in the discrete case. They consider the equivalence not only in the sense of equality between thermodynamical functions, but also in the sense of equality between all the correlation functions. Corrections, always in the discrete context for the grandcanonical and canonical ensembles, has been studied in [4].

For the relation between microcanonical and canonical ensembles in the thermodynamic limit we mention the seminal article of Lanford [13], and more recently [17].

We are interested here, for a system of finite  $N$  particles, in the difference between the microcanonical average of an observable  $A$  on a given energy shell (microcanonical

---

*Date:* August 27, 2017.

We thank Joel Lebowitz for pointing our attention to the microcanonical fluctuation formula of reference [14], that motivated the present work. This work has been partially supported by the European Advanced Grant *Macroscopic Laws and Dynamical Systems* (MALADY) (ERC AdG 246953) and by ANR grant LSD (ANR-15-CE40-0020-01). N.C. thanks Ceremade, Université Paris Dauphine for the kind hospitality.

manifold), and the canonical average of  $A$  at the corresponding temperature:

$$\Delta_N(A, u) = \langle A|u \rangle_N - \langle A \rangle_{N, \beta_N(u)} \quad (1.1)$$

where  $Nu$  is the value of the energy fixed in the microcanonical average, while  $\beta_N(u)$  is the corresponding inverse temperature determined such that the canonical average of the energy per particle is  $u$ . We will restrict our considerations to situations far from phase transitions (far from thermodynamic singularities).

By the law of large numbers we have a concentration of the canonical distribution of the energy per particle in the canonical distribution around the expected value. Since the microcanonical average is just a conditional expectation of the canonical average for a given value of the total energy, if  $A$  is uniformly bounded in  $N$ , or local, and the microcanonical expectation  $\langle A|u \rangle_N$  is enough regular in  $u$ ,  $\Delta_N(A, u) \rightarrow 0$ , as an easy consequence of a large deviation principle for the distribution of the energy under the canonical distribution (see [section 4](#)).

But here we are principally interested in *extensive observables*, like the total kinetic energy  $K_N$ , and their fluctuations in the microcanonical ensemble. In particular the microcanonical fluctuations of the total kinetic energy is greatly affected, and reduced, by the global constraint on the total energy and the asymptotic microcanonical variance, properly normalized, differs from the canonical one. In order to study such difference we need to compute explicitly the first order of  $\Delta_N(A, u)$ .

More precisely, let  $\langle K_N; K_N|u \rangle_N = \langle K_N^2|u \rangle_N - \langle K_N|u \rangle_N^2$ , the microcanonical variance of the kinetic energy, that typically has order  $N$ . The canonical variance of  $K_N$  depends only on the Maxwellian distribution on the velocities and is equal to  $Nn/(2\beta^2)$ , where  $n$  is the space dimension. It follows from the results contained in [section 5](#) that

$$\lim_{N \rightarrow \infty} \frac{1}{N} \langle K_N; K_N|u \rangle_N = \frac{n}{2\beta^2} \left( 1 - \frac{n}{2C(\beta)} \right) \quad (1.2)$$

where the energy  $u$  and inverse temperature  $\beta$  are connected by the thermodynamic relation, and  $C(\beta)$  is the heat capacity per particle, defined as  $C(\beta) = du(\beta)/d\beta^{-1}$ . Formula (1.2) was formally derived in [14] without controlling the error terms, and its rigorous derivation is the main motivation for the present article. Actually we prove (1.2) under some regularity conditions on the microcanonical expectations, and its finite  $N$  version, where we also compute explicitly the next order term (see formula (5.19)). We then provide one explicit example where these regularity conditions are satisfied, but we expect that they are verified for a large class of systems. Formula (1.2) is actually a consequence of a more general formula (5.2), also formally deduced in [14], that gives the explicit first order correction for  $\Delta_N(A, u)$ . Notice that our formula (5.17) for the first order correction differs from the one obtained in [14], for one term, see remark 5.4.

In the proof of (5.2) we use a strong form of the large deviations for the energy distribution under the canonical measure, i.e. the asymptotic expression (3.11) for the density of the canonical probability distribution of the energy. This strong *local* large deviation expression is proven in [section 3](#), as consequence of an Edgeworth expansion in the corresponding local central limit theorem. The expansion is obtained in [section 2](#) under the condition of uniform bounds in  $N$  for the first 4 derivatives of the free energy per particle  $f_N(\beta)$  of the canonical measure of the  $N$ -system, see (2.3).

Even though many of the arguments and results in sections 2,3 and 4 are well known in particular in the probabilistic literature, we decided to present this article as self contained as possible. For example the Edgeworth expansion argument we use in [section 2](#) is essentially the same as used in Feller book [9] for independent variables, but we could not find a precise reference for this statement for dependent continuous variables under canonical Gibbs distributions (for the discrete setting see [6], the general setting for dependent random variables is treated in [11]).

## 2. THE LOCAL CENTRAL LIMIT THEOREM AND ITS EDGEWORTH EXPANSION

Consider  $N$  particles, the momentum and coordinates given by  $\mathbf{p} := (p_1, \dots, p_N)$ ,  $p_i \in \mathbb{R}^n$  and  $\mathbf{q} := (q_1, \dots, q_N)$ ,  $q_i \in M$ , where  $M$  is a manifold of dimension  $n$ . The phase space is  $\Omega^N = (\mathbb{R}^n \times M)^N$ . Let  $\bar{\mathbf{q}}_i = (q_1, \dots, q_{i-1}, q_{i+1}, \dots, q_N)$  be the coordinates of all the particles except that of the  $i$  particle. To simplify the notation we take  $n = 1$ .

We want to consider systems whose Hamiltonian can be written as

$$H_N = \sum_{i=1}^N X_i$$

where

$$X_i := \frac{p_i^2}{2} + V(q_i, \bar{\mathbf{q}}_i) \quad i = 1, \dots, N$$

where  $V$  is a regular function. Define for  $\beta > 0$ :

$$f_N(\beta) := \frac{1}{N} \log \int_{\Omega^N} e^{-\beta H_N} d\mathbf{p} d\mathbf{q}.$$

Notice that the integration in the  $\mathbf{p}$  can always be done explicitly and

$$f_N(\beta) = \frac{1}{2} \log(2\pi\beta^{-1}) + \frac{1}{N} \log \int_{M^N} e^{-\beta \sum_i V(q_i, \bar{\mathbf{q}}_i)} d\mathbf{q}.$$

**Assumption:** We assume that there is an interval of values of  $\beta$  such that  $f_N(\beta)$  exists, together with its first four derivatives, and that are uniformly bounded in  $N$ :

$$\sup_N |f_N^{(j)}(\beta)| \leq C_\beta, \quad j = 0, 1, 2, 3, 4 \quad (2.1)$$

with  $C_\beta$  locally bounded in closed bounded intervals not including  $\beta = 0$ .

The canonical Gibbs measure associated to  $H_N$  and temperature  $\beta^{-1}$  is defined by

$$\nu_{\beta,N}(d\mathbf{p} d\mathbf{q}) = \exp\{-\beta H_N(\mathbf{p}, \mathbf{q}) - N f_N(\beta)\} d\mathbf{p} d\mathbf{q} \quad (2.2)$$

Defining  $h_N := H_N/N$ , direct calculations give:

$$\begin{aligned} f_N'(\beta) &= -\langle h_N \rangle_{\beta,N} = -u_N(\beta), \\ f_N''(\beta) &= N \langle (h_N - u_N(\beta))^2 \rangle_{\beta,N} \\ f_N'''(\beta) &= -N^2 \langle (h_N - u_N(\beta))^3 \rangle_{\beta,N} \\ f_N''''(\beta) &= N^3 \langle (h_N - u_N(\beta))^4 \rangle_{\beta,N} - 3N f_N''(\beta)^2. \end{aligned} \quad (2.3)$$

where we indicated  $\langle \cdot \rangle_{\beta,N}$  the average w.r.t. the canonical measure defined in (2.2).

Notice that, thanks to the presence of the kinetic energy,

$$\inf_N f_N''(\beta) := \sigma_-(\beta) > \frac{1}{2\beta^2}.$$

Define the centered energy

$$S_N := \sum_{j=1}^N (X_j - u_N(\beta))$$

and its characteristic function

$$\varphi_{\beta,N}(t) := \langle e^{it S_N} \rangle_{\beta,N}, \quad t \in \mathbb{R}. \quad (2.4)$$

By performing explicitly the integration over  $\mathbf{p}$ , we have

$$\varphi_{\beta,N}(t) = \left( \frac{1}{1 - it\beta^{-1}} \right)^{N/2} \langle e^{it \sum_j (V(q_j, \bar{q}_j) - v_N)} \rangle_{N,\beta}$$

where  $Nv_N = \langle \sum_j (V(q_j, \bar{q}_j)) \rangle_{N,\beta}$ . Consequently we have the bound:

$$|\varphi_{\beta,N}(t)| \leq \left( \frac{\beta^2}{t^2 + \beta^2} \right)^{\frac{N}{4}}, \quad (2.5)$$

thus  $|\varphi_{\beta,N}(t)| < 1$  for  $t \neq 0$  (i.e. is a characteristic function of a non-lattice distribution). Furthermore  $|\varphi_{\beta,N}(t)|$  is integrable for  $N \geq 3$ , and by the Fourier inversion theorem (see chapter XV.3 of [9]) the probability density function of the variable  $S_N$  exists for  $N \geq 3$ . Observe also that

$$\begin{aligned} \varphi'_{\beta,N}(0) &= 0, \quad \varphi''_{\beta,N}(0) = -N f_N''(\beta), \quad \varphi'''_{\beta,N}(0) = -iN f_N'''(\beta) \\ \varphi''''_{\beta,N}(0) &= N f_N''''(\beta) + 3N^2 f_N''(\beta)^2. \end{aligned} \quad (2.6)$$

In the following we denote the normal gaussian density by

$$\phi(x) = \frac{1}{\sqrt{2\pi}} e^{-x^2/2}.$$

Let  $\{H_j(x)\}_{j \geq 0}$  the Hermite polynomials defined by

$$\frac{d^j}{dx^j} \phi(x) = (-1)^j H_j(x) \phi(x) \quad (2.7)$$

The characteristic property of Hermite polynomials is that the Fourier transform of  $H_j(x)\phi(x)$  is given by

$$\int_{-\infty}^{+\infty} H_j(x) \phi(x) e^{itx} dx = (it)^j \hat{\phi}(t)$$

where  $\hat{\phi}(t) = e^{-\frac{t^2}{2}}$ . Recall that  $H_0 = 1$ ,  $H_1(x) = x$ ,  $H_3(x) = x^3 - 3x$ ,  $H_4(x) = x^4 - 6x^2 + 3$  and  $H_6(x) = x^6 - 15x^4 + 45x^2 - 15$ .

We can now state the Local Central Limit Theorem we need in the rest of the article.

**Theorem 2.1.** *Assume that  $\beta$  is such that the conditions (2.1) are satisfied. Define*

$$Y_N := \frac{\sum_{i=1}^N (X_i - u_N(\beta))}{\sqrt{N f_N''(\beta)}},$$

then the density distribution  $g_{\beta,N}(x)$  of  $Y_N$  for  $N \geq 3$  exists and as  $N \rightarrow \infty$

$$g_{\beta,N}(x) - \phi(x) - \phi(x) \left( \frac{Q_{\beta,N}^{(3)}(x)}{\sqrt{N}} + \frac{Q_{\beta,N}^{(4)}(x)}{N} \right) = o\left(\frac{1}{N}\right) K_N(\beta) \quad (2.8)$$

where

$$Q_{\beta,N}^{(3)}(x) = \frac{f_N'''(\beta)}{3! f_N''(\beta)^{\frac{3}{2}}} H_3(x) \quad (2.9)$$

$$Q_{\beta,N}^{(4)}(x) = \frac{f_N''''(\beta)}{4! f_N''(\beta)^2} H_4(x) + \frac{1}{2} \left( \frac{f_N'''(\beta)}{3! f_N''(\beta)^{\frac{3}{2}}} \right)^2 H_6(x) \quad (2.10)$$

and  $K_N(\beta)$  is bounded in  $N$ , uniformly on bounded closed intervals of  $\beta > 0$ .

*Proof.* We follow the proof of theorem 2 in chapter XVI.2 of [9] for independent random variables. By (2.5) and the Fourier inversion theorem the left hand side of (2.8) exists for  $N \geq 3$ . To simplify the notation we do not write the dependence on  $\beta$  of  $f_{\beta,N}$ ,  $\varphi_{\beta,N}$  and their derivatives. Consider the function

$$\widehat{\Phi}_N(t) = \varphi_N\left(\frac{t}{\sqrt{N f_N''}}\right) - e^{-\frac{t^2}{2}} \left[ 1 + P_N\left(\frac{it}{\sqrt{N f_N''}}\right) \right] \quad (2.11)$$

where  $\varphi_N(t/\sqrt{N f_N''})$  is the Fourier transform of  $g_{\beta,N}$  (see (2.4)) and  $P_N(it)$  is an appropriate polynomial in the variable  $it$ . We want to show that

$$\Delta_N = \int_{-\infty}^{\infty} |\widehat{\Phi}_N(t)| dt = o\left(\frac{1}{N}\right). \quad (2.12)$$

Choose  $\delta > 0$  arbitrary but fixed. There exists a number  $q_\delta < 1$  such that  $\left(\frac{\beta^2}{t^2 + \beta^2}\right)^{\frac{1}{4}} < q_\delta$  for  $|t| \geq \delta$ . The contribution of the intervals  $|t| > \delta \sqrt{N f_N''}$  to the integral (2.12), using (2.5), is bounded by

$$q_\delta^{N-3} \int_{-\infty}^{\infty} \left( \frac{\beta^2}{(t/\sqrt{N f_N''})^2 + \beta^2} \right)^3 dt + \int_{|t| > \delta \sqrt{N f_N''}} e^{-\frac{t^2}{2}} \left| P_N\left(\frac{it}{\sqrt{N f_N''}}\right) \right| dt \quad (2.13)$$

and this tends to zero more rapidly than any power of  $1/N$ .

We now estimate the contribution to  $\Delta_N$  from the region  $|t| \leq \delta \sqrt{N f_N''}$ . Let us rewrite

$$\Delta_N = \int_{-\infty}^{\infty} e^{-\frac{t^2}{2}} \left| e^{\psi_N\left(\frac{t}{\sqrt{N f_N''}}\right)} - 1 - P_N\left(\frac{it}{\sqrt{N f_N''}}\right) \right| dt \quad (2.14)$$

where<sup>1</sup>

$$\psi_N(t) = \log \varphi_N(t) + \frac{1}{2} N f_N'' t^2.$$

The function  $\psi_N(t)$  is four times differentiable and in  $t = 0$  its derivatives are given by

<sup>1</sup>For a complex number  $z$  such that  $|z| < 1$ , we define  $\log(1+z) = \sum_n \frac{(-z)^n}{n}$ .

$$\begin{aligned}
\psi'_N(t) &= \frac{\varphi'_N(t)}{\varphi_N(t)} + N f'_N t, & \psi'_N(0) &= 0. \\
\psi''_N(t) &= \frac{\varphi''_N(t)}{\varphi_N(t)} - \frac{\varphi'_N(t)^2}{\varphi_N(t)^2} + N f''_N, & \psi''_N(0) &= 0. \\
\psi'''_N(t) &= \frac{\varphi'''_N(t)}{\varphi_N(t)} - \frac{\varphi'_N(t)\varphi''_N(t)}{\varphi_N(t)^2} - \frac{2\varphi'_N(t)\varphi''_N(t)}{\varphi_N(t)^2} + \frac{2\varphi'_N(t)^3}{\varphi_N(t)^3}, & \psi'''_N(0) &= -iN f'''_N. \\
\psi''''_N(t) &= \frac{\varphi''''_N(t)}{\varphi_N(t)} - \frac{3\varphi'_N(t)\varphi'''_N(t)}{\varphi_N(t)^2} - \frac{3\varphi''_N(t)^2}{\varphi_N(t)^2} + \frac{4\varphi'_N(t)^2\varphi''_N(t)}{\varphi_N(t)^3} + \frac{6\varphi'_N(t)^2\varphi''_N(t)}{\varphi_N(t)^3} - \frac{6\varphi'_N(t)^4}{\varphi_N(t)^4} \\
& \psi''''_N(0) = \varphi''''_N(0) - 3\varphi''_N(0)^2 = N f''''_N.
\end{aligned}$$

where we used relations (2.6). Let  $(it)^2\gamma_N(it)$  be the Taylor approximation for  $\psi_N(t)/N$ . Where  $\gamma_N(it)$  is a polynomial of degree 2 with  $\gamma_N(0) = 0$ ; it is uniquely determined by the property

$$\psi_N(t) - N(it)^2\gamma_N(it) = No(|t|^4) \quad (2.15)$$

and it is given by

$$\gamma_N(it) := \frac{f'''_N}{3!} it + \frac{f''''_N}{4!} (it)^2$$

We choose

$$P_N(it) := \sum_{k=1}^2 \frac{1}{k!} [N(it)^2\gamma_N(it)]^k$$

then  $P_N(it)$  is a polynomial in the variable  $it$  with real coefficients depending on  $N$  and  $\beta$ . We use the inequality

$$\left| e^\alpha - 1 - \sum_{k=1}^2 \frac{\beta^k}{k!} \right| \leq |e^\alpha - e^\beta| + \left| e^\beta - 1 - \sum_{k=1}^2 \frac{\beta^k}{k!} \right| \leq e^\gamma \left( |\alpha - \beta| + \frac{|\beta|^3}{3!} \right)$$

with  $\gamma = \max\{|\alpha|, |\beta|\}$ . Furthermore we choose  $\delta$  so small that for  $|t| < \delta$

$$|\psi_N(t) - N(it)^2\gamma_N(it)| \leq \epsilon (f''_N)^2 N |t|^4$$

and

$$|\psi_N(t)| < N \frac{1}{4} f''_N t^2 \quad |\gamma_N(it)| \leq a_N |t| \leq \frac{1}{4} f''_N$$

provided that  $a_N > 1 + |f''_N|$ . For  $|t| < \delta\sqrt{Nf''_N}$  the integrand in (2.14) can be bounded by

$$e^{-\frac{1}{4}t^2} \left( \epsilon \frac{t^4}{N} + \frac{a_N^3}{3!} \left( \frac{|t|^3}{\sqrt{Nf''_N}} \right)^3 \right) \quad (2.16)$$

As  $\epsilon$  is arbitrary we have that (2.12) is proved. The function  $\Phi_N(t)$  defined in (2.11) is the Fourier transform of

$$g_{\beta,N}(x) - \phi(x) - \phi(x) \sum_{k=1}^8 b_{Nk} H_k(x) \quad (2.17)$$

where  $b_{Nk}$  are appropriate coefficients depending on  $N$  and  $H_k(x)$  are the Hermite polynomials defined in (2.7). If we rearrange the terms of the sum in ascending powers of  $1/\sqrt{N}$  we get an expression of the form postulated in the theorem plus terms involving powers  $1/N^k$  with  $k > 1$  that can be dropped and obtain the result.  $\square$

The same argument leads to higher order expansions, but the terms cannot be expressed by simple explicit formulas. We have the following

**Theorem 2.2.** *Assume that  $f_N''(\beta), \dots, f_N^{(k)}(\beta)$  exist and are uniformly bounded in  $N$ . Define*

$$Y_N := \frac{\sum_{i=1}^N (X_i - u_N(\beta))}{\sqrt{N f_N''(\beta)}}$$

then the density distribution  $g_{\beta,N}(x)$  of  $Y_N$  for  $N \geq 3$  exists and as  $N \rightarrow \infty$

$$g_{\beta,N}(x) - \phi(x) - \phi(x) \sum_{j=3}^k \frac{1}{N^{\frac{1}{2}j-1}} Q_{\beta,N}^{(j)}(x) = o\left(\frac{1}{N^{\frac{1}{2}k-1}}\right) \quad (2.18)$$

uniformly in  $x$ . Here  $\phi(x)$  is the standard normal density,  $Q_{\beta,N}^{(j)}$  is a real polynomial depending only on  $f_N''(\beta), \dots, f_N^{(k)}(\beta)$ , and whose coefficients are uniformly bounded in  $N$ .

Note that Theorem 2.1 is Theorem 2.2 for  $k = 4$  and taking  $k > 4$  does not improve our estimates and results.

**Remark 2.3.** *Theorem 2.1 is stated for continuous random variables  $X_i$ . It can be stated also for discrete random variables, in the same form once  $|\varphi_{\beta,N}(t)|$ , the characteristic function of  $S_N$ , is integrable. In spin systems with finite range interacting potentials, like the Ising model, this is the case, see [7] and [4] where a Gaussian upper bound on the characteristic function is proved.*

### 3. LOCAL LARGE DEVIATIONS AND BOLTZMANN FORMULA

In this section we study the energy distribution under the canonical measure. With reasonable conditions on the interaction potential  $V$ ,  $f_N(\beta)$  is finite for every  $\beta > 0$ . We can extend its definition to all  $\beta \in \mathbb{R}$  denoting  $f_N(\beta) = +\infty$  for  $\beta \leq 0$ .

We define the Legendre-Fenchel transform of  $f_N(\beta)$ :

$$f_{N*}(u) := \sup_{\beta} \{-\beta u - f_N(\beta)\} = \sup_{\beta > 0} \{-\beta u - f_N(\beta)\} \quad (3.1)$$

Let  $\mathcal{D}_{f_N}, \mathcal{D}_{f_{N*}}$  the corresponding domain of definition. For any  $u \in \mathcal{D}_{f_{N*}}$  there exists a unique  $\beta \in \mathcal{D}_{f_N}$  such that

$$u = -f_N'(\beta) \quad \text{and} \quad \beta = -f_{N*}'(u). \quad (3.2)$$

Under the canonical measure (2.2)  $h_N$  can be seen as a normalized sum of random variables. We denote by  $\mathcal{F}_{N,\beta}(u)$  the density of its probability distribution. For any integrable function  $F: \mathbb{R} \rightarrow \mathbb{R}$

$$\int_{\Omega^N} F(h_N) d\nu_{\beta,N} = \int_{\mathbb{R}} F(u) \mathcal{F}_{N,\beta}(u) du = \int_{\mathbb{R}} F(u) e^{-N[\beta u + f_N(\beta)]} W_N(u) du \quad (3.3)$$



where

$$W_N(u) := \frac{d}{du} \int_{h_N \leq u} d\mathbf{p}d\mathbf{q} \quad (3.4)$$

**Theorem 3.1.** *Let  $u \in \mathcal{D}_{f_{N^*}}$  and  $\gamma = -f'_{N^*}(u)$  defined by (3.2) be such that  $f_N(\gamma)$  satisfies (2.1). Then, for large  $N$ ,*

$$W_N(u) = e^{-Nf_{N^*}(u)} \sqrt{\frac{N f''_{N^*}(u)}{2\pi}} \left( 1 + \frac{Q_{\gamma, N}^{(4)}(0)}{N} + o\left(\frac{1}{N}\right) K_N(\gamma) \right) \quad (3.5)$$

where  $K_N(\gamma)$  and  $Q_{\gamma, N}^{(4)}(0)$  are defined in (2.8) and (2.10) respectively.

*Proof.* Let  $\omega = (\mathbf{p}, \mathbf{q}) \in \Omega^N$ ,  $\mathbf{X}(\omega) = (X_1(\omega), \dots, X_N(\omega))$ , and  $\mathbf{x} = (x_1, \dots, x_N) \in \mathbb{R}^N$ . Consider the positive measure  $\alpha_N(d\mathbf{x})$  on  $\mathbb{R}^N$  defined, for any integrable function  $F$  on  $\mathbb{R}^N$ , by

$$\int_{\Omega^N} F(\mathbf{X}(\omega)) d\omega = \int_{\mathbb{R}^N} F(\mathbf{x}) \alpha_N(d\mathbf{x}) \quad (3.6)$$

so that for any  $\gamma$  we have

$$\int_{\Omega^N} F(\mathbf{X}(\omega)) \nu_{\gamma, N}(d\omega) = \int_{\mathbb{R}^N} F(\mathbf{x}) e^{-\gamma \sum_{i=1}^N x_i - Nf_N(\gamma)} \alpha_N(d\mathbf{x}) \quad (3.7)$$

For any integrable function  $G : \mathbb{R} \rightarrow \mathbb{R}$  we can write

$$\int_{\mathbb{R}^N} G\left(\frac{1}{N} \sum_{j=1}^N x_j\right) \alpha_N(d\mathbf{x}) = \int_{-\infty}^{+\infty} G(s) W_N(s) ds \quad (3.8)$$

Take  $u \in \mathcal{D}_{f_{N^*}}$  and  $\gamma \in \mathcal{D}_{f_N}$  as in the hypotheses of the theorem. For any integrable function  $G : \mathbb{R} \rightarrow \mathbb{R}$  we have

$$\begin{aligned} & \int_{\mathbb{R}^N} G\left(\frac{1}{N} \sum_{j=1}^N (x_j - u)\right) e^{-\gamma \sum_{j=1}^N x_j - Nf_N(\gamma)} \alpha_N(d\mathbf{x}) \\ &= \int_{\mathbb{R}} G\left(\frac{s - u}{\sqrt{f''_N(\gamma)}}\right) e^{-\gamma N s - Nf_N(\gamma)} W_N(s) ds \\ &= e^{Nf_{N^*}(u)} \sqrt{f''_N(\gamma)} \int_{\mathbb{R}} G(y) e^{-\gamma N \sqrt{f''_N(\gamma)} y} W_N(\sqrt{f''_N(\gamma)} y + u) dy. \end{aligned}$$

In order to apply theorem 2.1 we identify

$$e^{Nf_{N^*}(u)} \sqrt{f''_N(\gamma)} e^{-\gamma N \sqrt{f''_N(\gamma)} y} W_N(\sqrt{f''_N(\gamma)} y + u) = \sqrt{N} g_{\gamma, N}(\sqrt{N} y)$$

so that for  $y = 0$

$$e^{Nf_{N^*}(u)} \sqrt{f''_N(\gamma)} W_N(u) = \sqrt{N} g_{\gamma, N}(0) = \sqrt{\frac{N}{2\pi}} \left( 1 + \frac{Q_{\gamma, N}^{(4)}(0)}{N} + o\left(\frac{1}{N}\right) K_N(\gamma) \right). \quad (3.9)$$

Since  $f''_N(\gamma) = 1/f''_{N^*}(u)$ , (3.5) follows directly.  $\square$

We can resume the above result more explicitly, by using the bounds and the explicit form of the polynomial  $Q_{\gamma,N}^{(4)}(0) = \frac{\gamma}{4} f_N'''(\gamma)$ ,

$$\left| W_N(u) e^{N f_{N^*}(u)} \sqrt{\frac{2\pi}{N f_{N^*}''(u)}} - 1 \right| \leq \frac{\gamma C_\gamma}{4N} + o\left(\frac{1}{N}\right) K_N(\gamma). \quad (3.10)$$

Theorem 3.1 allows to write the probability density function in (3.3) as

$$\mathcal{F}_{N,\beta}(u) = e^{-N I_{N,\beta}(u)} \sqrt{\frac{N}{2\pi} f_{N^*}''(u)} \left( 1 + \frac{Q_{\gamma(u),N}^{(4)}(0)}{N} + o\left(\frac{1}{N}\right) K_N(\gamma(u)) \right) \quad (3.11)$$

where  $\gamma(u) = -f_{N^*}'(u)$  and

$$I_{N,\beta}(u) := \beta u + f_N(\beta) + f_{N^*}(u) = \beta(u - u_N(\beta)) - f_{N^*}(u_N(\beta)) + f_{N^*}(u). \quad (3.12)$$

As  $\beta = -f_{N^*}'(u_N(\beta))$ , we can thus rewrite

$$I_{N,\beta}(u) := f_{N^*}(u) - f_{N^*}(u_N(\beta)) - f_{N^*}'(u_N(\beta))(u - u_N(\beta)). \quad (3.13)$$

The functional  $I_{N,\beta}(u)$  is convex, derivable and has a minimum in  $u_N(\beta)$  where  $u_N(\beta) := \langle h_N \rangle_{\beta,N}$ ,

$$I'_{N,\beta}(u_N(\beta)) = 0,$$

and

$$I''_{N,\beta}(u_N(\beta)) = f_{N^*}''(u_N(\beta)) = 1/f_N''(\beta).$$

Equation (3.11) says that the sequence  $h_N$  satisfies a local large deviation principle, also called *Large Deviation Principle in the Strong Form*, see [6] where the principle is defined for discrete random variables with assumptions that are generally stronger than (2.1).

#### 4. MICROCANONICAL DISTRIBUTION AND EQUIVALENCE OF ENSEMBLES.

We here define the equivalence of ensembles. Given an observable  $A$  on  $\Omega_N$ , we define the microcanonical average  $\langle A|u \rangle_N$  as a conditional expectation by the classic formula:

$$\langle AF(h_N) \rangle_{N,\beta} = \langle \langle A|h_N \rangle F(h_N) \rangle_{N,\beta} = \int F(u) \langle A|u \rangle_N \mathcal{F}_{N,\beta}(u) du, \quad (4.1)$$

for any measurable function  $F(u)$  on  $\mathbb{R}$ . It is an easy exercise to see that these conditional expectations do not depend on  $\beta$ . Of course (4.1) defines the conditional expectation only a.s. with respect to the Lebesgue measure. But under the regularity assumptions on the interaction potential  $V$ , the microcanonical surface

$$\Sigma_N(u) = \{(\mathbf{p}, \mathbf{q}) \in \Omega_N : h_N = u\} \quad (4.2)$$

is regular enough such that the change of variables (co-area formulas cf. [12]) can be applied and give the existence of a regular conditional distribution on  $\Sigma_N(u)$ , defined for every value of  $u$ . We will assume in the following various conditions on the function  $u \mapsto \langle A|u \rangle_N$ , that have to be verified in the various applications.

By equivalence of ensembles we mean here the convergence of

$$\langle A \rangle_{\beta,N} - \langle A|u_N(\beta) \rangle_N \xrightarrow{N \rightarrow \infty} 0, \quad (4.3)$$

for a certain class of functions. We are in particular interested in the rate of convergence in (4.3).

For the case when  $A$  is a bounded function such that  $\langle A|u \rangle_N$  is continuous around  $u = u_N(\beta)$  uniformly in  $N$ , this is a quite straightforward consequence of the upper bound on large deviations. By the uniform continuity of  $\langle A|u \rangle_N$ , for any  $\epsilon > 0$ , there exists  $\delta_\epsilon > 0$  such that  $|\langle A|u \rangle_N - \langle A|u_N(\beta) \rangle_N| < \epsilon$  if  $|u - u_N(\beta)| < \delta_\epsilon$ . Then

$$|\langle A \rangle_{\beta,N} - \langle A|u_N(\beta) \rangle_N| \leq 2\|A\|_\infty \int_{|u-u_N(\beta)| \geq \delta_\epsilon} \mathcal{F}_{N,\beta}(u) du + \epsilon$$

Let us split the large deviation term:

$$\int_{|u-u_N(\beta)| \geq \delta_\epsilon} \mathcal{F}_{N,\beta}(u) du = \int_{u > u_N(\beta) + \delta_\epsilon} \mathcal{F}_{N,\beta}(u) du + \int_{u < u_N(\beta) - \delta_\epsilon} \mathcal{F}_{N,\beta}(u) du.$$

We estimate the first term of the RHS of the above expression.. By the exponential Chebychef inequality, for any  $\lambda > 0$ :

$$\int_{u > \bar{u}} \mathcal{F}_{N,\beta}(u) du \leq e^{-N[\lambda(u_N(\beta) + \delta_\epsilon) - f_N(\beta - \lambda) + f_N(\beta)]}.$$

Notice that, using (3.1) and (3.12),

$$I_{N,\beta}(\bar{u}) = \sup_{\beta - \lambda} (\lambda \bar{u} - f_N(\beta - \lambda)) + f_N(\beta) \quad \bar{u} = u_N(\beta) + \delta_\epsilon \quad (4.4)$$

Consequently optimizing the estimate over  $\beta - \lambda > 0$ ,  $\lambda > 0$  we have

$$\int_{u > \bar{u}} \mathcal{F}_{N,\beta}(u) du \leq e^{-NI_{N,\beta}(\bar{u})}.$$

Analogously applying exponential Chebychef inequality on the second term we have

$$I_{N,\beta}(\bar{u}) = \sup_{\beta + \lambda > 0} (\lambda \bar{u} - f_N(\beta + \lambda)) + f_N(\beta) \quad \bar{u} = u_N(\beta) - \delta_\epsilon$$

and a similar estimate can be obtained.

Condition (2.1) on  $f_N''(\beta)$  implies the strong convexity of  $I_{N,\beta}(\bar{u})$  in an interval around  $u_N(\beta)$ , uniform in  $N$ . For any  $\beta > 0$  there exist  $\delta > 0$  such that

$$I_{N,\beta}(u_N(\beta) \pm \delta) \geq \frac{\delta^2}{2C_\beta} \quad (4.5)$$

It follows that

$$\int_{|u-u_N(\beta)| \geq \delta_\epsilon} \mathcal{F}_{N,\beta}(u) du \leq 2e^{-N\delta_\epsilon^2/2C_\beta} \quad (4.6)$$

that converges exponentially to 0 for any  $\epsilon > 0$ . Taking  $\epsilon \rightarrow 0$  concludes the argument. In the next section we will analyze closer this convergence, allowing observables  $A$  that are extensive.

## 5. LEBOWITZ-PERCUS-VERLET FORMULAS FOR FLUCTUATIONS

In this section  $A$  is a function on  $\Omega_N$ , eventually extensive. We define  $\|A\|_{p,\beta,N}$  the  $L^p$ -norm of  $A$  with respect to the canonical measure  $\nu_{\beta,N}$ .

We assume that for every  $\beta > 0$  in the same interval of (2.1) and  $b_\beta > 0$ , the observable  $A$  satisfies the following relations:

(i) There exists a positive constant  $C_\beta$  and a small number  $\epsilon > 0$  such that

$$\begin{aligned} \|A\|_{4,\beta,N} &\leq C_\beta \|A\|_{2,\beta,N} < +\infty \\ |\langle A|u_N(\beta)\rangle_N| &\leq C_\beta \|A\|_{2,\beta,N}, \\ \left| \frac{d}{du} \langle A|u\rangle_N \Big|_{u_N(\beta)} \right| &\leq C_\beta N^{1/2} \|A\|_{2,\beta,N}, \\ \left| \frac{d^2}{du^2} \langle A|u\rangle_N \Big|_{u_N(\beta)} \right| &\leq C_\beta N^{1-\epsilon} \|A\|_{2,\beta,N}. \end{aligned}$$

(ii) If  $\delta_N := b_\beta \sqrt{\frac{\log N}{N}}$  there exists a positive constant  $C_\beta$  such that

$$B_{N,\beta} := \sup_{|u-u_N(\beta)| \leq \delta_N} \left| \frac{d^3}{du^3} \langle A|u\rangle_N \right| \leq \frac{C_\beta \sqrt{N}}{\log N} \|A\|_{2,\beta,N}. \quad (5.1)$$

**Theorem 5.1.** *Assume conditions (i)-(ii) above. Then, for  $N$  large enough, the following formula holds*

$$\langle A|u_N(\beta)\rangle_N = \langle A \rangle_{\beta,N} - \frac{1}{2N} \frac{d}{d\beta} \left[ \frac{1}{f_N''(\beta)} \frac{d}{d\beta} \langle A \rangle_{\beta,N} \right] + o\left(\frac{1}{N}\right) \|A\|_{2,\beta,N}. \quad (5.2)$$

*Proof.* In the proof  $C_\beta$  will be a generic constant depending on  $\beta$ . Since expression (5.2) is homogeneous in  $A$ , we can divide by  $\|A\|_{2,\beta,N}$  and consider functions  $A$  such that  $\|A\|_{2,\beta,N} = 1$ . We write the difference between the canonical and microcanonical expectations as

$$\langle A \rangle_{\beta,N} - \langle A|u_N(\beta)\rangle_N = \int \mathcal{F}_{N,\beta}(u) [\langle A|u\rangle_N - \langle A|u_{\beta,N}\rangle_N] du \quad (5.3)$$

Denote

$$\begin{aligned} G_N(u) &= \langle A|u\rangle_N - \langle A|u_N(\beta)\rangle_N - \frac{d}{du} \langle A|u\rangle_N \Big|_{u_N(\beta)} (u - u_N(\beta)) \\ &\quad - \frac{1}{2} \frac{d^2}{du^2} \langle A|u\rangle_N \Big|_{u_N(\beta)} (u - u_N(\beta))^2 \end{aligned} \quad (5.4)$$

Obviously  $G_N(u_N(\beta)) = G'_N(u_N(\beta)) = G''_N(u_N(\beta)) = 0$ . We want to prove that

$$\int \mathcal{F}_{N,\beta}(u) G_N(u) du \sim o\left(\frac{1}{N}\right). \quad (5.5)$$

Under conditions (i) above and using (2.1), the properties of the norm and Schwarz inequality, we have that  $\|G_N\|_{2,\beta,N}^2 \leq C'_\beta$ .

Let  $\delta_N = b_\beta \sqrt{\frac{\log N}{N}}$  be the sequence of assumption (ii) above. Due to the strong convexity of  $I_{N,\beta}(u)$ , by (4.6), we have  $I_{N,\beta}(u) \geq \delta_N^2 / (2C_\beta)$  for  $N$  large enough. We

choose  $b_\beta$  such that  $b_\beta^2/(2C_\beta) > 4$ . This last condition will be clear at the end of the proof.

Consider the bounded function

$$G_{N,\delta_N}(u) = G_N(u)1_{[|u-u_N(\beta)|<\delta_N]}.$$

We can split the integral and, using Schwarz inequality, obtain

$$\begin{aligned} \left| \int \mathcal{F}_{N,\beta}(u) G_N(u) du \right| &\leq \sqrt{C'_\beta} \left( \int \mathcal{F}_{N,\beta}(u) 1_{[|u-u_N(\beta)|\geq\delta_N]} du \right)^{1/2} \\ &\quad + \left| \int \mathcal{F}_{N,\beta}(u) G_{N,\delta_N}(u) du \right| \end{aligned}$$

By (4.5) and the above choice of  $\delta_N$  the integral of the first term can be bounded by

$$\int \mathcal{F}_{N,\beta}(u) 1_{[|u-u_N(\beta)|\geq\delta_N]} du \leq 2N^{-\frac{b_\beta^2}{2C_\beta}}. \quad (5.6)$$

As  $b_\beta^2/(2C_\beta) > 4$ , the first term on the RHS is of order  $o(1/N)$ .

For the second term, by Jensen's inequality and (3.11), for any  $\alpha > 0$  we have

$$\begin{aligned} \left| \int \mathcal{F}_{N,\beta}(u) G_{N,\delta_N}(u) du \right| &\leq \frac{1}{\alpha N} \log \int e^{\alpha N G_{N,\delta_N}(u)} \mathcal{F}_{N,\beta}(u) du \\ &= \frac{1}{\alpha N} \log \left[ \int_{[|u-u_N(\beta)|<\delta_N]} e^{-N(I_{N,\beta}(u) - \alpha G_{N,\delta_N}(u))} \sqrt{\frac{N}{2\pi}} f''_{N^*}(u) (1 + \dots) du + 2N^{-\frac{b_\beta^2}{2C_\beta}} \right]. \end{aligned}$$

Since, by Taylor formula and condition (ii) above,  $|G_{N,\delta_N}(u)| \leq B_{N,\beta} |u - u_N(\beta)|^3$ , and  $I_{N,\beta}(u) \geq a_\beta (u - u_N(\beta))^2$  as  $|u - u_N(\beta)| < \delta_N$ , we have that

$$\begin{aligned} I_{N,\beta}(u) - \alpha G_{N,\delta_N}(u) &\geq (u - u_N(\beta))^2 (a_\beta - \alpha B_{N,\beta} |u - u_N(\beta)|) \\ &\geq (u - u_N(\beta))^2 (a_\beta - \alpha B_{N,\beta} \delta_N) \end{aligned} \quad (5.7)$$

Choose now a sequence  $\alpha_N \rightarrow \infty$ , for  $N \rightarrow \infty$ , and such that  $\alpha_N B_{N,\beta} \delta_N < 1/(2C_\beta)$ . We have consequently that

$$I_{N,\beta}(u) - \alpha_N G_{N,\delta_N}(u) \geq 0, \quad \text{if } |u - u_N(\beta)| < \delta_N.$$

Then we have:

$$\begin{aligned} &N \left| \int \mathcal{F}_{N,\beta}(u) G_{N,\delta_N}(u) du \right| \\ &\leq \frac{1}{\alpha_N} \log \left[ 2\delta_N \sqrt{\frac{N}{2\pi}} \sup_{|u-u_N(\beta)|<\delta_N} \sqrt{f''_{N^*}(u)} (1 + \dots) + 2N^{-a_\beta b_\beta^2} \right] \\ &= \frac{1}{\alpha_N} \log \left[ b_\beta \sqrt{\log N} \sqrt{\frac{2}{\pi}} \sup_{|u-u_N(\beta)|<\delta_N} \sqrt{f''_{N^*}(u)} (1 + \dots) + 2N^{-a_\beta b_\beta^2} \right]. \end{aligned}$$

We choose  $\alpha_N$  growing faster than  $\log \log N$  and this last term will go to 0. Since  $B_{N,\beta} \delta_N \leq \frac{C}{\sqrt{\log N}}$ , it is enough to choose  $\alpha_N := c\sqrt{\log N}$  for  $c$  small enough to have  $\alpha_N B_{N,\beta} \delta_N < 1/(2C_\beta)$  satisfied.

We can thus rewrite equation (5.3) as

$$\langle A \rangle_{\beta, N} = \langle A | u_N(\beta) \rangle_N + \frac{f_N''(\beta)}{2N} \frac{d^2}{du^2} \langle A | u \rangle_N \Big|_{u=u_N(\beta)} + o\left(\frac{1}{N}\right). \quad (5.8)$$

Note that for any differentiable function  $g(u)$

$$\frac{d}{du} g(u) \Big|_{u=u_N(\beta)} = -\frac{1}{f_N''(\beta)} \frac{d}{d\beta} g(u_N(\beta)) \quad (5.9)$$

$$f_N''(\beta) \frac{d^2}{du^2} g(u) \Big|_{u=u_N(\beta)} = \frac{d}{d\beta} \left[ \frac{1}{f_N''(\beta)} \frac{d}{d\beta} g(u_N(\beta)) \right]. \quad (5.10)$$

By (5.10) we can write (5.8) as

$$\langle A | u_N(\beta) \rangle_N = \langle A \rangle_{\beta, N} - \frac{1}{2N} \frac{d}{d\beta} \left[ \frac{1}{f_N''(\beta)} \frac{d}{d\beta} \langle A | u_N(\beta) \rangle_N \right] + o\left(\frac{1}{N}\right). \quad (5.11)$$

By lemma 5.2 below and condition (ii) above:

$$\frac{1}{N} \frac{d}{d\beta} \left[ \frac{1}{f_N''(\beta)} \frac{d}{d\beta} \left( \langle A \rangle_{\beta, N} - \langle A | u_N(\beta) \rangle_N \right) \right] \sim o\left(\frac{1}{N}\right)$$

and (5.2) follows.  $\square$

**Lemma 5.2.** *Under the conditions of Theorem 5.1 the following relations hold*

$$\begin{aligned} \frac{d}{d\beta} \left( \langle A \rangle_{\beta, N} - \langle A | u_N(\beta) \rangle_N \right) &= \frac{f_N'''(\beta)}{2N} \frac{d^2}{du^2} \langle A | u \rangle_N \Big|_{u=u_N(\beta)} + o_N(1) \|A\|_{2, \beta, N} \\ \frac{d^2}{d\beta^2} \left( \langle A \rangle_{\beta, N} - \langle A | u_N(\beta) \rangle_N \right) &= \frac{f_N''''(\beta)}{2N} \frac{d^2}{du^2} \langle A | u \rangle_N \Big|_{u=u_N(\beta)} + o_N(1) \|A\|_{2, \beta, N} \end{aligned} \quad (5.12)$$

where  $o_N(1) \rightarrow 0$  as  $N \rightarrow \infty$ .

*Proof.* As in the previous proof, we can assume that  $\|A\|_{2, \beta, N} = 1$ . Note that by (5.3)

$$\begin{aligned} &\frac{d}{d\beta} \left( \langle A \rangle_{\beta, N} - \langle A | u_N(\beta) \rangle_N \right) \\ &= -N \int \left( \langle A | u \rangle_N - \langle A | u_N(\beta) \rangle_N \right) (u - u_N(\beta)) \mathcal{F}_{\beta, N}(u) du - \frac{d}{d\beta} \langle A | u_N(\beta) \rangle_N, \end{aligned} \quad (5.13)$$

and, the definition (5.4) of  $G_N(u)$  and (5.5), this is equal to

$$\begin{aligned} &= -f_N''(\beta) \frac{d}{du} \langle A | u \rangle_N \Big|_{u=u_N(\beta)} - \frac{d}{d\beta} \langle A | u_N(\beta) \rangle_N + \frac{f_N'''(\beta)}{2N} \frac{d^2}{du^2} \langle A | u \rangle_N \Big|_{u=u_N(\beta)} \\ &\quad - N \int G_N(u) (u - u_N(\beta)) \mathcal{F}_{\beta, N}(u) du \\ &= \frac{f_N'''(\beta)}{2N} \frac{d^2}{du^2} \langle A | u \rangle_N \Big|_{u=u_N(\beta)} - N \int G_N(u) (u - u_N(\beta)) \mathcal{F}_{\beta, N}(u) du. \end{aligned}$$

In order to estimate the last term on the right hand side of the above relation, define

$$\tilde{G}_{N, \delta_N}(u) := N G_N(u) (u - u_N(\beta)) 1_{\{|u - u_N(\beta)| \leq \delta_N\}}.$$

Then dividing the integral we have

$$N \int G_N(u) (u - u_N(\beta)) \mathcal{F}_{\beta,N}(u) du = \int_{[|u-u_N(\beta)| \leq \delta_N]} \tilde{G}_{N,\delta_N}(u) \mathcal{F}_{\beta,N}(u) du \\ + N \int_{[|u-u_N(\beta)| > \delta_N]} G_N(u) (u - u_N(\beta)) \mathcal{F}_{\beta,N}(u) du.$$

The first term can be easily estimated by condition (5.1) and Taylor formula as

$$|\tilde{G}_{N,\delta_N}(u)| \leq N C_\beta \frac{\delta_N^3}{\sqrt{\log N}} = C_\beta b_\beta^3 \frac{\log N}{\sqrt{N}}.$$

For the second integral we use Schwarz inequality so that

$$N \int_{[|u-u_N(\beta)| > \delta_N]} G_N(u) (u - u_N(\beta)) \mathcal{F}_{\beta,N}(u) du \\ \leq N \|G_N\|_{2,\beta,N} \left( \int_{[|u-u_N(\beta)| > \delta_N]} (u - u_N(\beta))^2 \mathcal{F}_{\beta,N}(u) du \right)^{1/2} \\ \leq N \|G_N\|_{2,\beta,N} \left( \int_{[|u-u_N(\beta)| > \delta_N]} (u - u_N(\beta))^4 \mathcal{F}_{\beta,N}(u) du \right)^{1/4} \left( \int_{[|u-u_N(\beta)| > \delta_N]} \mathcal{F}_{\beta,N}(u) du \right)^{1/4} \\ \leq C_\beta N \frac{1}{N^{1/2}} N^{-a_\beta b_\beta^2/4} = C N^{-\frac{a_\beta b_\beta^2}{4} + \frac{1}{2}},$$

where we used (2.1), (2.3), (5.6). The condition  $a_\beta b_\beta^2 > 4$  assures the convergence to 0 as  $N \rightarrow \infty$ . This proves the first of (5.12).

For the second one, deriving (5.13) once more in  $\beta$  and using (2.3), we obtain

$$\frac{d^2}{d\beta^2} \left( \langle A \rangle_{\beta,N} - \langle A | u_N(\beta) \rangle_N \right) \\ = N^2 \int (\langle A | u \rangle_N - \langle A | u_N(\beta) \rangle_N) (u - u_N(\beta))^2 \mathcal{F}_{\beta,N}(u) du \\ - N f_N''(\beta) \left( \langle A \rangle_{\beta,N} - \langle A | u_N(\beta) \rangle_N \right) - \frac{d^2}{d\beta^2} \langle A | u_N(\beta) \rangle_N. \quad (5.14)$$

Using again definition (5.4) of  $G_N(u)$  we have that (5.14) is equal to

$$N^2 \frac{d}{du} \langle A | u \rangle_N \Big|_{u=u_N(\beta)} \int (u - u_N(\beta))^3 \mathcal{F}_{\beta,N}(u) du \\ + \frac{N^2}{2} \frac{d^2}{du^2} \langle A | u \rangle_N \Big|_{u=u_N(\beta)} \int (u - u_N(\beta))^4 \mathcal{F}_{\beta,N}(u) du \\ - \frac{1}{2} \frac{d^2}{du^2} \langle A | u \rangle_N \Big|_{u=u_N(\beta)} (f_N''(\beta))^2 - \frac{d^2}{d\beta^2} \langle A | u_N(\beta) \rangle_N \\ + N^2 \int G_N(u) (u - u_N(\beta))^2 \mathcal{F}_{\beta,N}(u) du + N \int G_N(u) \mathcal{F}_{\beta,N}(u) du \quad (5.15)$$

The first 4 terms of (5.15) are equal to

$$\begin{aligned}
& -f_N'''(\beta) \frac{d}{du} \langle A|u \rangle_N \Big|_{u=u_N(\beta)} + \left( \frac{1}{2N} f_N''''(\beta) + \frac{3}{2} (f_N''(\beta))^2 \right) \frac{d^2}{du^2} \langle A|u \rangle_N \Big|_{u=u_N(\beta)} \\
& - \frac{1}{2} (f_N''(\beta))^2 \frac{d^2}{du^2} \langle A|u \rangle_N \Big|_{u=u_N(\beta)} - \frac{d^2}{d\beta^2} \langle A|u_N(\beta) \rangle_N \\
& = -f_N'''(\beta) \frac{d}{du} \langle A|u \rangle_N \Big|_{u=u_N(\beta)} + \frac{1}{2N} f_N''''(\beta) \frac{d^2}{du^2} \langle A|u \rangle_N \Big|_{u=u_N(\beta)} \\
& + (f_N''(\beta))^2 \frac{d^2}{du^2} \langle A|u \rangle_N \Big|_{u=u_N(\beta)} - \frac{d^2}{d\beta^2} \langle A|u_N(\beta) \rangle_N \\
& = \frac{f_N'''(\beta)}{f_N''(\beta)} \frac{d}{d\beta} \langle A|u_N(\beta) \rangle_N + \frac{1}{2N} f_N''''(\beta) \frac{d^2}{du^2} \langle A|u \rangle_N \Big|_{u=u_N(\beta)} \\
& + f_N''(\beta) \frac{d}{d\beta} \frac{1}{f_N''(\beta)} \frac{d}{d\beta} \langle A|u_N(\beta) \rangle_N - \frac{d^2}{d\beta^2} \langle A|u_N(\beta) \rangle_N \\
& = \frac{1}{2N} f_N''''(\beta) \frac{d^2}{du^2} \langle A|u \rangle_N \Big|_{u=u_N(\beta)}.
\end{aligned}$$

where we used (5.9), (5.10). We consider now the last two terms of (5.15). To estimate the first one define

$$\hat{G}_{N,\delta_N}(u) := N^2 G_N(u) (u - u_N(\beta))^2 \mathbf{1}_{\{|u - u_N(\beta)| \leq \delta_N\}}.$$

Then, by (5.1) we have that  $|\hat{G}_{N,\delta_N}(u)| \leq C_\beta N^2 \delta_N^5$  and

$$\left| \int \hat{G}_{N,\delta_N}(u) \mathcal{F}_{\beta,N}(u) du \right| \leq C_\beta N^2 \delta_N^6 = C_\beta \frac{(\log N)^3}{N}.$$

While using Schwarz inequality twice we get

$$\begin{aligned}
& \left| \int_{\{|u - u_N(\beta)| > \delta_N\}} N^2 G_N(u) (u - u_N(\beta))^2 \mathcal{F}_{\beta,N}(u) du \right| \\
& \leq N^2 \|G_N\|_{4,\beta,N} \|u - u_N(\beta)\|_{4,\beta,N}^2 \left( \int_{\{|u - u_N(\beta)| > \delta_N\}} \mathcal{F}_{\beta,N}(u) du \right)^{1/4} \\
& \leq C_\beta N^2 \frac{1}{N} \frac{1}{N^{a_\beta b_\beta^2/4}} = C_\beta N^{-\frac{a_\beta b_\beta^2}{4} + 1}
\end{aligned}$$

that is of  $o_N(1)$  since  $a_\beta b_\beta^2 > 4$ . By (5.5) the last term in (5.15) is  $o_N(1)$ . This proves the second of (5.12).  $\square$

Let  $A$  and  $B$  two functions such that they and their product satisfies the assumptions of Theorem (5.1). Applying formula (5.2) to  $AB$  we obtain

$$\langle AB|u_N(\beta) \rangle_N = \langle AB \rangle_{N,\beta} - \frac{1}{2N} \frac{d}{d\beta} \left[ \frac{1}{f_N''(\beta)} \frac{d \langle AB \rangle_{N,\beta}}{d\beta} \right] + o\left(\frac{1}{N}\right) \|AB\|_{2,\beta,N}.$$



while

$$\begin{aligned} \langle A|u_N(\beta)\rangle_N \langle B|u_N(\beta)\rangle_N &= \langle A\rangle_{N,\beta} \langle B\rangle_{N,\beta} - \frac{1}{2N} \left( \langle A\rangle_{N,\beta} \frac{d}{d\beta} \left[ \frac{1}{f_N''(\beta)} \frac{d\langle B\rangle_{N,\beta}}{d\beta} \right] + \right. \\ &\quad \left. + \langle B\rangle_{N,\beta} \frac{d}{d\beta} \left[ \frac{1}{f_N''(\beta)} \frac{d\langle A\rangle_{N,\beta}}{d\beta} \right] \right) + C_N \\ &= \frac{1}{N} \frac{1}{f_N''(\beta)} \frac{d\langle A\rangle_{N,\beta}}{d\beta} \frac{d\langle B\rangle_{N,\beta}}{d\beta} - \frac{1}{2N} \frac{d}{d\beta} \left[ \frac{1}{f_N''(\beta)} \frac{d(\langle A\rangle_{N,\beta} \langle B\rangle_{N,\beta})}{d\beta} \right] + C_N \end{aligned}$$

where  $C_N$  contains all term of smaller order and is bounded by

$$|C_N| \leq o\left(\frac{1}{N}\right) \|A\|_{2,\beta,N} \|B\|_{2,\beta,N}.$$

Then defining the correlations

$$\begin{aligned} \langle A; B|u_N(\beta)\rangle_N &:= \langle AB|u_N(\beta)\rangle_N - \langle A|u_N(\beta)\rangle_N \langle B|u_N(\beta)\rangle_N, \\ \langle A; B\rangle_{\beta,N} &:= \langle AB\rangle_{\beta,N} - \langle A\rangle_{\beta,N} \langle B\rangle_{\beta,N}, \end{aligned} \quad (5.16)$$

we get the formula for the equivalence of the correlations:

$$\begin{aligned} \langle A; B|u_N(\beta)\rangle_N &= \langle A; B\rangle_{N,\beta} - \frac{1}{N} \frac{1}{f_N''(\beta)} \frac{d\langle A\rangle_{N,\beta}}{d\beta} \frac{d\langle B\rangle_{N,\beta}}{d\beta} - \frac{1}{2N} \frac{d}{d\beta} \left[ \frac{1}{f_N''(\beta)} \frac{d\langle A; B\rangle_{N,\beta}}{d\beta} \right] \\ &\quad + o\left(\frac{1}{N}\right) (\|AB\|_{2,\beta,N} + \|A\|_{2,\beta,N} \|B\|_{2,\beta,N}). \end{aligned} \quad (5.17)$$

**Remark 5.3.** This formula is different than the one of reference [14]. The term with the derivative of the canonical correlation is in general smaller than the others. It can be even smaller than the error term as we will see evaluating the fluctuations of the kinetic energy below.

**Remark 5.4.** For extensive variables, like  $A = \sum_{i=1}^N p_i^2$ , typically we have  $\|A\|_{2,\beta,N} \sim N$ , that implies that the error in (5.17) is of order  $o(N)$ . But in these cases the other terms are of order  $N$ .

**5.1. Fluctuations of kinetic energy.** Consider the kinetic energy

$$K(\mathbf{p}) = \sum_{j=1}^N \frac{p_j^2}{2}.$$

Then, if  $n$  is the space dimension,

$$\langle K\rangle_{N,\beta} = \frac{Nn}{2\beta}, \quad \langle K^2\rangle_{N,\beta} = \frac{N(N+2)n^2}{4\beta^2} \quad \langle K; K\rangle_{N,\beta} = \frac{Nn^2}{2\beta^2}$$

and

$$\frac{d\langle K\rangle_{N,\beta}}{d\beta} = -\frac{Nn}{2\beta^2}, \quad \frac{d\langle K; K\rangle_{N,\beta}}{d\beta} = -\frac{Nn^2}{\beta^3}$$

applying equation (5.17) we obtain

$$\begin{aligned} \langle K; K|u_N(\beta)\rangle_N - \langle K; K\rangle_{N,\beta} &= -\frac{n^2 N}{4\beta^4 f_N''(\beta)} + \frac{1}{2} \frac{d}{d\beta} \left( \frac{n^2}{f_N''\beta^3} \right) \\ &+ o\left(\frac{1}{N}\right) (\|K^2\|_{2,\beta,N} + \|K\|_{2,\beta,N}^2). \end{aligned} \quad (5.18)$$

Observe that as  $\|K\|_{2,\beta,N} \sim N/\beta$  and  $\|K^2\|_{2,\beta,N} \sim N^2/\beta^2$  the second term in the r.h.s of (5.18) is smaller than the error term. Dividing by  $N$ , we obtain for the variances of  $K/\sqrt{N}$ :

$$\frac{1}{N} \langle K; K|u_N(\beta)\rangle_N = \frac{n}{2\beta^2} - \frac{n^2}{4\beta^4 f_N''(\beta)} + o_N(1) = \frac{n}{2\beta^2} \left( 1 - \frac{n}{2C_N(\beta)} \right) + o_N(1) \quad (5.19)$$

The quantity  $C_N(\beta) = \beta^2 f_N''(\beta)$  is called heat capacity (per particle). This is in fact equal to  $\frac{d}{d\beta^{-1}} u_N(\beta)$ . Notice that (5.19) coincide, up to terms of lower order in  $N$ , to formula (3.7) in [14].

In particular the asymptotic canonical and microcanonical variances of  $\frac{1}{\sqrt{N}} K_N$  are different. Denoting by  $V$  the total potential energy, since  $K + V$  is constant under the microcanonical measure, we have that  $\langle K; K|u_N(\beta)\rangle_N = \langle V; V|u_N(\beta)\rangle_N$ , so the same formula is valid for  $\langle V; V|u_N(\beta)\rangle_N$ .

It remains to prove the conditions of theorem 5.1 are satisfied by  $\langle K_N; K_N|u\rangle_N$ , but this in general depends on the model considered, i.e. on the interaction between the particles.

In section 3 we have defined

$$W_N(u) = \frac{d}{du} \Omega_N(u)$$

where

$$\Omega_N(u) = \int_{\mathbb{R}^N} d\mathbf{p} \int_{\mathbb{R}^N} d\mathbf{q} \theta(N(u - h_N(\mathbf{p}, \mathbf{q})))$$

where the Heaviside unit step function  $\theta(x)$  is defined by  $\theta(x) = 0$  for  $x < 0$  and  $\theta(x) = 1$  for  $x \geq 0$ . Using the  $N$ -spherical coordinates on the momentum variables, this can be written as

$$\begin{aligned} \Omega_N(u) &= S_{N-1} \int_{\mathbb{R}^N} d\mathbf{q} \int_0^\infty \rho^{N-1} \theta\left(Nu - \frac{\rho^2}{2} - V(\mathbf{q})\right) d\rho \\ &= S_{N-1} \int_{\mathbb{R}^N} d\mathbf{q} \theta(Nu - V(\mathbf{q})) \int_0^{\sqrt{2(Nu - V(\mathbf{q}))}} \rho^{N-1} d\rho \\ &= S_{N-1} \frac{2^{N/2}}{N} \int_{\mathbb{R}^N} d\mathbf{q} (Nu - V(\mathbf{q}))^{\frac{N}{2}} \theta(Nu - V(\mathbf{q})) \end{aligned}$$

where  $S_{N-1} = 2\pi^{N/2}/\Gamma(N/2)$  is the surface of the  $N - 1$  dimensional unit sphere. Consequently

$$W_N(u) = \frac{(2\pi)^{N/2} N}{\Gamma(N/2)} \int_{\mathbb{R}^N} d\mathbf{q} (Nu - V(\mathbf{q}))^{\frac{N}{2}-1} \theta(Nu - V(\mathbf{q})) \quad (5.20)$$

This formula goes back to Gibbs ([2], chapter 8, (308)), and one can prove that  $W_N(u)$  is at least  $\lceil \frac{N}{2} - 1 \rceil$  times differentiable see [8].

For any observable  $A$ , the microcanonical mean can be written as

$$\langle A | u \rangle_N = \frac{\frac{\partial}{\partial u} \int d\mathbf{p} d\mathbf{q} \theta(Nu - H(\mathbf{p}, \mathbf{q})) A(\mathbf{p}, \mathbf{q})}{W_N(u)} \quad (5.21)$$

Using the  $N$  dimensional spherical momentum coordinates as above, one can write the microcanonical mean of the kinetic energy as

$$\begin{aligned} \langle K | u \rangle_N &= W_N(u)^{-1} \left( \frac{(2\pi)^{N/2} N}{\Gamma(N/2)} \int_{\mathbb{R}^N} d\mathbf{q} (Nu - V(\mathbf{q}))^{\frac{N}{2}} \theta(Nu - V(\mathbf{q})) \right) \\ &= \frac{N^2 \Omega_N(u)}{2W_N(u)} = \frac{\int_{\mathbb{R}^N} d\mathbf{q} (Nu - V(\mathbf{q}))^{\frac{N}{2}} \theta(Nu - V(\mathbf{q}))}{\int_{\mathbb{R}^N} d\mathbf{q} (Nu - V(\mathbf{q}))^{\frac{N}{2}-1} \theta(Nu - V(\mathbf{q}))} \end{aligned}$$

Of course we have the trivial bound  $\langle K | u \rangle_N \leq Nu$ . Furthermore, since the microcanonical distribution is symmetric in the  $\{p_j, j = 1, \dots, N\}$ , we have

$$\frac{1}{2} \langle p_j^2 | u \rangle_N = \frac{2 \int_{\mathbb{R}^N} d\mathbf{q} (Nu - V(\mathbf{q}))^{\frac{N}{2}} \theta(Nu - V(\mathbf{q}))}{N \int_{\mathbb{R}^N} d\mathbf{q} (Nu - V(\mathbf{q}))^{\frac{N}{2}-1} \theta(Nu - V(\mathbf{q}))} \quad (5.22)$$

An analogous calculation brings to

$$\langle K^2 | u \rangle_N = \frac{2^2 \int_{\mathbb{R}^N} d\mathbf{q} (Nu - V(\mathbf{q}))^{\frac{N}{2}+1} \theta(Nu - V(\mathbf{q}))}{\int_{\mathbb{R}^N} d\mathbf{q} (Nu - V(\mathbf{q}))^{\frac{N}{2}-1} \theta(Nu - V(\mathbf{q}))} \quad (5.23)$$

We can rewrite these expression by using the microcanonical potential energy weight:

$$\widetilde{W}_N(v) := \frac{d}{dv} \int_{\mathbb{R}^N} \theta(Nv - V(\mathbf{q})) d\mathbf{q}. \quad (5.24)$$

then

$$\langle K | u \rangle_N = N \frac{2 \int_0^u (u-v)^{\frac{N}{2}} \widetilde{W}_N(v) dv}{\int_0^u (u-v)^{\frac{N}{2}-1} \widetilde{W}_N(v) dv}$$

and

$$\langle K^2 | u \rangle_N = 4N^2 \frac{2 \int_0^u (u-v)^{\frac{N}{2}+1} \widetilde{W}_N(v) dv}{\int_0^u (u-v)^{\frac{N}{2}-1} \widetilde{W}_N(v) dv}. \quad (5.25)$$

The formulas above imply that these microcanonical averages are at least  $\lceil N/2 \rceil$  times differentiable in  $u$  and the derivatives can be explicitly computed.

Starting from expression (5.23) we give a qualitative argument to understand why conditions (i)-(iii) in section 5 should be satisfied for extensive observables. We then present an example where most calculations can be made exactly. From (5.23) one can see that dimensionally the microcanonical mean of  $K^2$  behaves as  $N^2 u^2$  and that the derivatives with respect to  $u$  are well defined till the order  $N/2 - 1$ . The third derivative of  $\langle K^2 | u \rangle_N$  behaves dimensionally as  $N^2/u$ . Thus, as the canonical norm  $\|K\|_{2,\beta,N}^2 = N(N+2)/(4\beta)$  and  $u_N(\beta)$  does not grow in  $N$ , the required conditions are,

at least dimensionally, satisfied. The same reasoning can be extended to any extensive or intensive quantity looking directly expression (5.21).

**5.2. Exactly solvable one dimensional model.** We here introduce the one dimensional model system studied in [8] where conditions (5.1) can be explicitly satisfied.

Consider  $N$  identical point particles confined by a one dimensional box of size  $L$ . The Hamiltonian is

$$H(\mathbf{p}, \mathbf{q}) = \sum_{i=1}^N \frac{p_i^2}{2m} + V(\mathbf{q}) = E \quad (5.26)$$

The potential energy  $V = V_{\text{int}} + V_{\text{box}}$  is determined by the interaction potential

$$V_{\text{int}}(\mathbf{q}) = \frac{1}{2} \sum_{\substack{i,j=1 \\ i \neq j}}^N V_{\text{pair}}(|q_i - q_j|)$$

and the box potential

$$V_{\text{box}}(\mathbf{q}) = \begin{cases} 0 & \mathbf{q} \in [0, L]^N \\ +\infty & \text{otherwise.} \end{cases}$$

The pair potential is given by

$$V_{\text{pair}}(r) = \begin{cases} \infty & r \leq d_{hc} \\ -U_0 & d_{hc} < r < d_{hc} + r_0 \\ 0 & r \geq d_{hc} + r_0 \end{cases}$$

where  $d_{hc} > 0$  is the hard core diameter of a particle with respect to pair interactions. The pair potential above can be viewed as a simplified Lennard-Jones potential. The depth of the potential well is determined by the binding energy parameter  $U_0 > 0$  and the interaction range by the parameter  $r_0$ . It is assumed

$$0 < r_0 \leq d_{hc}$$

the latter condition ensures that particles may interact with their nearest neighbors only. In order to have the volume sufficiently large for realizing the completely dissociated state, corresponding to  $V = 0$  it is  $L > L_{\text{min}} \equiv (N - 1)(d_{hc} + r_0)$ . The energy  $E$  of the system can take values between the ground state energy  $E_0 = -(N - 1)U_0$  and infinity. Following the calculations of [8] expression (5.23) for this model becomes

$$\langle K^2 | u \rangle_N = \frac{\sum_{k=0}^{N-1} \omega_k (Nu + kU_0)^{\frac{N}{2}+1} \theta(Nu + kU_0)}{\sum_{k=0}^{N-1} \omega_k (Nu + kU_0)^{\frac{N}{2}-1} \theta(Nu + kU_0)} \quad (5.27)$$

where  $\omega_k$  are positive coefficient depending on  $N$  and  $L$  see [8] for more details. Furthermore the canonical mean energy per particle

$$u_N(\beta) = \frac{1}{2\beta} - \frac{U_0}{N} \frac{\sum_{k=0}^{N-1} k \omega_k e^{-\beta k U_0}}{\sum_{k=0}^{N-1} \omega_k e^{-\beta k U_0}},$$

so that

$$\frac{1}{2\beta} - U_0 \leq u_N(\beta) \leq \frac{1}{2\beta} \quad (5.28)$$

Expression (5.27) shows that  $\langle K^2 | u \rangle_N$  does not vanish iff at least  $u + \frac{N-1}{N}U_0 \geq 0$  this implies  $u + U_0 > 0$ . Expression (5.27) is explicit but complicate. To verify that  $\langle K^2 | u \rangle_N$  satisfies conditions (i)-(iii) we consider the particular case of  $-(N-2)/N \leq u < -(N-3)/N$ . As only the last two terms are present in the sums, expression (5.27) becomes

$$\langle K^2 | u \rangle_N = \frac{\omega_{N-1} + \omega_{N-2} \left(1 - \frac{1}{N} \frac{U_0}{u+U_0}\right)^{N/2+1}}{\omega_{N-1} + \omega_{N-2} \left(1 - \frac{1}{N} \frac{U_0}{u+U_0}\right)^{N/2-1}} N^2 (u + U_0)^2$$

where we use to simplify the formulas  $u + \frac{N-1}{N}U_0 \sim u + U_0$  for  $N$  large. Calculating the derivatives of (5.27) (we omit the boring calculation) one can show that there exists a positive constant  $A$  such that

$$\begin{aligned} \langle K^2 | u \rangle_N &\leq N^2 (u + U_0)^2 \\ \left| \frac{d}{du} \langle K^2 | u \rangle_N \right| &\leq A N^2 (u + U_0) \\ \left| \frac{d^2}{du^2} \langle K^2 | u \rangle_N \right| &\leq A N^2 \left( \frac{U_0}{u + U_0} + \frac{U_0^2}{(u + U_0)^2} \right) \\ \left| \frac{d^3}{du^3} \langle K^2 | u \rangle_N \right| &\leq A N^2 \left[ \frac{U_0}{(u + U_0)^2} + \frac{U_0^2}{(u + U_0)^3} + \frac{U_0^3}{(u + U_0)^4} \right] \end{aligned} \quad (5.29)$$

Remembering that

$$\langle K^2 \rangle_{N,\beta} = \frac{N(N+2)}{4\beta^2}$$

by (5.28) and (5.29) conditions (i)-(iii) of theorem 5.1 are satisfied.

## 6. THERMODYNAMIC LIMIT

All the statements in the previous sections are for finite  $N$ . We here recall the classical Lanford results in the thermodynamic limit [13], under the assumption that  $f_N(\beta)$  is bounded in  $N$  along with the first four derivatives.

By definition  $f_N(\beta)$  is analytical in  $\beta$ . Assume now that  $f_N(\beta)$  converges to  $z(\beta)$  which is analytical in  $\beta$ . Then all the derivatives of  $f_N(\beta)$  converge to the derivatives of  $z(\beta)$  and conditions (2.1) are satisfied. We thus have

$$f'_N(\beta) \rightarrow z'(\beta) = -u(\beta), \quad f''_N(\beta) \rightarrow z''(\beta) = \chi(\beta)$$

Usual thermodynamic notations denote  $F(\beta^{-1}) = -\beta^{-1}z(\beta)$  the *free energy*,  $\chi(\beta)$  *heat capacity*, and  $s(u) = -z^*(u) = -\lim_{N \rightarrow \infty} f_{N^*}(u)$  the *thermodynamic entropy*. It follows the Boltzmann formula:

$$s(u) = \lim_{N \rightarrow \infty} \frac{1}{N} \log W_N(u) \quad (6.1)$$

Also we denote

$$I_\beta(u) = \lim_{N \rightarrow \infty} I_{\beta,N}(u) = \beta u - s(u) + z(\beta) \quad (6.2)$$

that is the rate function for the large deviations of  $h_N$  in the infinite Gibbs state defined by DLR equations.

In absence of phase transition, i.e.  $I_\beta(u) = 0$  only for  $u = z'(\beta)$ , then the equivalence on ensembles follows from (5.3). Differentiability of the limit of  $f_N(\beta)$  depends on the

system we are considering. In next section we give examples where analyticity of  $z(\beta)$  is assured at least for  $\beta$  small enough.

## 7. EXAMPLES

**7.1. Independent case.** Consider a system of  $N$  noninteracting particles in a potential. This is the case  $V(q_i, \bar{\mathbf{q}}_i) = V(q_i)$ . The Hamiltonian can be written as the sum of  $N$  identical terms

$$H_N(\mathbf{p}, \mathbf{q}) = \sum_{i=1}^N h(p_i, q_i). \quad (7.1)$$

Consequently  $f_N(\beta)$  does not depend on  $N$  and is a smooth function of  $\beta$  if  $V$  is a nice reasonable potential.

**7.1.1. Independent harmonic oscillators.** Consider a system of  $N$  harmonic oscillators in dimension  $d$ . The Hamiltonian is given by

$$H = \sum_{i=1}^N \left[ \frac{p_i^2}{2} + \frac{q_i^2}{2} \right]. \quad (7.2)$$

To simplify notations take  $n = 1$ . Explicitely we have

$$f(\beta) = \log(2\pi\beta^{-1})$$

and  $z'(\beta) = -\beta^{-1}$ ,  $z''(\beta) = \beta^{-2}$ , so that the heat capacity here is  $z''(\beta)\beta^2 = 1$ .

If we calculate the expected value of the kinetic energy  $K$  with respect to the canonical measure at inverse temperature  $\beta$  we obtain

$$\langle K \rangle_\beta = \frac{N}{2\beta}. \quad (7.3)$$

The fluctuations (the *variance*) of  $K$  are given by

$$\langle K; K \rangle_\beta = \frac{N}{2\beta^2}. \quad (7.4)$$

The expected value of  $K$  with respect to the microcanonical measure is given by

$$\langle K|u \rangle_N = \frac{Nu}{2} \quad (7.5)$$

and

$$\langle K^2|u \rangle_N = \frac{N+2}{4(N+1)} (Nu)^2. \quad (7.6)$$

This imply that the microcanonical variance is given by

$$\langle K; K|u \rangle_N = \langle K^2|u \rangle_N - \langle K|u \rangle_N^2 = \frac{(Nu)^2}{4(N+1)}. \quad (7.7)$$

Since  $\langle h_N \rangle_\beta = u_N(\beta) = \frac{1}{\beta}$ , we have

$$\langle K; K|u_N(\beta) \rangle_N - \langle K; K \rangle_{N,\beta} = \frac{N^2}{4(N+1)\beta^2} - \frac{N}{2\beta^2} = -\frac{N}{4\beta^2} \left( 1 + \frac{1}{N+1} \right), \quad (7.8)$$

that coincide with the general formula (5.18).

**7.2. Mean Field.** We consider the Hamiltonian

$$h_N = \frac{1}{N} \sum_1^N \frac{p_i^2}{2} + \frac{1}{N^2} \sum_{i,j=1}^N V(q_i, q_j), \quad (7.9)$$

where  $V$  is a symmetric reasonable potential such that  $\int e^{-\beta V} dq_1 dq_2 < +\infty$  for any  $\beta > 0$ . One can check by direct computation, using the symmetry of the potential that  $f_N^{(j)}(\beta)$  are uniformly bounded in  $N$ .

**7.3. One dimensional chain of oscillators.** A very common model is an unpinned chain of anharmonic oscillators of Fermi-Pasta-Ulam type, whose hamiltonian is given by

$$H_N = \sum_1^N \left[ \frac{p_i^2}{2} + V(q_i - q_{i-1}) \right] \quad (7.10)$$

with various boundary conditions. Defining  $r_i = q_i - q_{i-1}$ , we are back to the independent case.

**7.4. Real Gas.** Consider a system of  $N$  particles interacting with a stable and tempered pair potential  $V: \mathbb{R}^d \rightarrow \mathbb{R} \cup \{\infty\}$ , i.e., there exists  $B \geq 0$  such that:

$$\sum_{1 \leq i < j \leq N} V(q_i - q_j) \geq -BN$$

for all  $N$  and all  $q_1, \dots, q_N$  and the integral

$$C(\beta) = \int_{\mathbb{R}^d} |e^{-\beta V(q)} - 1| dq$$

is convergent for some  $\beta > 0$  (and hence for all  $\beta > 0$ ). In [16] it has been proved the validity of cluster expansion for the canonical partition function in the high temperature - low density regime. This implies that the thermodynamic free energy is analytic in  $\beta$  if  $\beta$  and the density are small enough. Conditions (2.1) are thus satisfied.

**7.5. Unbounded spin systems with finite range potential.** We consider here the unbounded spin systems studied in [3]. For any domain  $\Lambda$  of  $\mathbb{Z}^d$ , with  $|\Lambda| = N$ , we consider the following ferromagnetic Hamiltonian on the phase space  $\mathbb{R}^\Lambda$  defined as follows

$$H_N(\mathbf{q}) = \sum_{j=1}^N \left[ \phi(q_j) + \sum_{i \sim j} V(q_i, q_j) \right] = \sum_{j=1}^N X_j,$$

where  $i \sim j$  means that the sum is over the sites that are at distance  $R > 0$  from  $j$ . Here  $\phi$  is a one particle phase on  $\mathbb{R}$  with at least quadratic increase at infinity,  $V$  is a convex function on  $\mathbb{R}$  with bounded second derivative, i.e.  $|V''(t)| \leq C$ . As the kinetic energy term is not present to use Theorem 2.2 we need to prove that the characteristic function  $\varphi_N(t)$  of the centered energy has modulus  $|\varphi_N(t)| < 1$  and  $|\varphi_N(t)|$  is integrable. We have to prove an analogous of (2.5) which assures that the probability density function of the variable  $S_N$  exists. The finite range of the potential is sufficient to prove both properties. Define a  $\Lambda_R \subset \Lambda$

$$\Lambda_R = \{i \in \Lambda : d(i, j) > 2R\},$$

and

$$Y_k = \phi(q_k) + 2 \sum_{i \sim k} V(q_i, q_k).$$

We can write the Hamiltonian as

$$H_N(\mathbf{q}) = \sum_{k \in \Lambda_R} Y_k + H_{\Lambda \setminus \Lambda_R},$$

where  $H_{\Lambda \setminus \Lambda_R}$  depends only on the variables in  $\Lambda \setminus \Lambda_R$ . For any  $\Lambda \subset \mathbb{Z}^d$ , let  $\nu_{\beta, \Lambda}$  be the canonical measure defined by the Hamiltonian defined above and indicate by  $E_{\beta, \Lambda}$  the expected value w.r.t.  $\nu_{\beta, \Lambda}$ . Then

$$\begin{aligned} \varphi_N(t) &= E_{\beta, \Lambda}(e^{it \sum_{k \in \Lambda_R} Y_k + it H_{\Lambda \setminus \Lambda_R}}) = E_{\beta, \Lambda}(e^{it H_{\Lambda \setminus \Lambda_R}} E_{\beta, \Lambda_R}(e^{it \sum_{k \in \Lambda_R} Y_k})) \\ &= E_{\beta, \Lambda}(e^{it H_{\Lambda \setminus \Lambda_R}} \prod_{k=1}^{|\Lambda_R|} E_{\beta, k}(e^{it Y_k})), \end{aligned}$$

where in the last equality we used independence of the  $\{Y_k\}$  variables due to the finite range potential. We thus have

$$|\varphi_N(t)| \leq E_{\beta, \Lambda}(\prod_{k=1}^{|\Lambda_R|} |E_{\beta, k}(e^{it Y_k})|) = E_{\beta, \Lambda}(\prod_{k=1}^{|\Lambda_R|} |\varphi_k(t)|).$$

The variables  $\{Y_k\}$  have finite probability density. This implies that their characteristic functions  $\{\varphi_k(t)\}$  have modulus strictly less than one for  $t \neq 0$  (see [9]). Furthermore such density is in  $L^2$  so that, by Plancherel equality,  $|\varphi_k(t)|^2$  is integrable (see [9]). These two properties of  $\varphi_k(t)$  assure that the modulus of  $\varphi_N(t)$  is strictly less than one for  $t \neq 0$  and integrable for  $|\Lambda_R|$  large enough so that, by the Fourier inversion theorem, the probability density function of the centered energy exists.

In [3] exponential decay of correlations is proven for  $\beta$  small enough which implies analyticity of the free energy in the thermodynamic limit.

#### REFERENCES

- [1] Boltzmann L., "Über die eigenschaften monozyklischer und anderer damit verwandter Systeme", in *Wissenschaftliche Abhandlungen* (C. F. Hasenöhl New York, ed.), Vol. III, 1968.
- [2] J. W. Gibbs, *Elementary Principles in Statistical Mechanics* (r. b. D. Yale University Press New York, ed.), 1902.
- [3] T. Bodineau and B. Helffer, *The log-Sobolev inequality for unbounded spin systems*, J. Funct. Anal. **166** (1999), no. 1, 168–178.
- [4] N. Cancrini and F. Martinelli, *Comparison of finite volume Gibbs measures under mixing condition*, Markov Processes. Rel. Fields **6** (2000), 1–49.
- [5] P. Diaconis and D. Friedman, *A dozen De Finetti-style results in search of a theory*, Ann. Inst. H. Poincaré, Probabilités et Statistiques **23** (1987), 397–423.
- [6] R. L. Dobrushin and B. Shlosman, *Large and Moderate Deviations in the Ising Model*, Adv. Soviet Math. **20** (1994), 1–130.
- [7] R. L. Dobrushin and B. Tirozzi, *The Central Limit Theorem and the Problem of Equivalence of Ensembles*, Comm. Math. Phys. **54** (1977), 173–192.
- [8] J. Dunkel and S. Hilbert, *Phase Transitions in small systems: Microcanonical vs. canonical ensembles*, Physica A **370** (2006), 390–406.
- [9] Feller W., *An introduction to probability theory and its applications*, 3rd ed. (Wiley, ed.), Vol. II, 1971.
- [10] Khinchin A. Ia, *Mathematical foundations of statistical mechanics*.



- [11] I. A. Ibragimov and Yu. V. Linnik, *Independent and Stationary Random Variables* (G. Wolters-Noordhoff, ed.), 1971.
- [12] L. Evans and R. Gariepy, *Measure Theory and Fine Properties of Functions* (CRC, ed.), 1992.
- [13] O. E. Lanford, *Entropy and equilibrium states in classical statistical mechanics* (A. Lenard, ed.), Springer Berlin Heidelberg, Berlin, Heidelberg, 1973.
- [14] J. L. Lebowitz, J. K. Percus, and L. Verlet, *Ensemble Dependence of Fluctuations with Applications to Machine Computations*, Phys. Rev **153** (1967), no. 1, 250–254.
- [15] S. Olla, *Large Deviations*, Appunti lezioni (2013).
- [16] E. Pulvirenti and D. Tsagkarogiannis, *Cluster Expansion in the Canonical Ensemble*, Commun. Math. Phys. **316** (2012), 289–306.
- [17] D. W. Stroock and O. Zeitouni, *Microcanonical distributions, Gibbs states, and the equivalence of ensembles*, Festschrift in honour of F. Spitzer. Birkhauser (1991), 399–424.

NICOLETTA CANCRINI, DIIIIE UNIVERSITÀ. L'AQUILA, 1-67100 L'AQUILA, ITALY  
*E-mail address:* nicoleтта.cancrini@univaq.it

STEFANO OLLA, CEREMADE, UMR-CNRS, UNIVERSITÉ PARIS DAUPHINE, PSL RESEARCH UNIVERSITY,  
75016 PARIS, FRANCE.  
*E-mail address:* olla@ceremade.dauphine.fr