On the equivalence of thermodynamics ensembles for flexible polymer chains

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HIGHLIGHTS

- The equivalence between Gibbs and Helmholtz ensembles for (not confined) polymer chains has been investigated.
- We rigorously proved the equivalence for a class of polymer models characterized by a continuous pairing interaction.
- We have introduced an original method based on the stationary phase technique.

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ABSTRACT

Although the problem of the ensembles equivalence for flexible polymers has aroused considerable interest, there is not an overall consensus on this topic. In this work, we present a theoretical investigation on the asymptotic equivalence of two ensembles for single flexible polymer chains (without confinement effects, i.e. fluctuating in the entire space): the first is the Gibbs (or isotensional) ensemble with one end-terminal of the chain tethered to a given point and the other subjected to an applied force; the other ensemble is the Helmholtz (or isometric) one characterized by both terminals tethered to fixed points. The equivalence property is rigorously proved for a class of potentials characterized by a continuous pairing interaction between neighboring monomers. To approach the problem we adopted an original analytical formalism based on the stationary phase technique and on the exact determination of the eigenvalues sign of the Hessian matrix of the phase function. To give some examples of application, the general result is successively applied to freely-jointed chains, to flexible polymers with extensible bonds and to chains with domains that exhibit conformational transitions between two stable states.

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1. Introduction

The problem of ensembles equivalence plays a central role in the assessment of the basic foundations of statistical mechanics. It consists in determining whether, in the thermodynamic limit (number of degrees of freedom approaching infinity), two statistical ensembles are equivalent, i.e. they lead to the same mathematical form of the constitutive equation describing the system under investigation (at equilibrium) [1–3]. Similarly, the equivalence can be also characterized by a Legendre transformation between the thermodynamic potentials (free energies) of the conjugated variables or by a Laplace–Stieltjes transformation between the partition functions of the conjugated ensembles [1].

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As an example, we can mention the microcanonical and canonical ensembles, representing the two most important statistical descriptions of many-particle systems. As initially observed by Gibbs, their definitions, in general, do not guarantee the equivalence in the thermodynamic limit [4]. Therefore, many theoretical studies have been conducted in order to understand how the equivalence property depends on the system considered, i.e. on the type of interaction acting among the particles [5–7]. It has been recently shown that the ensemble inequivalence can be observed in several systems with long-range interactions [8–10]. In particular, this behavior has been studied for generalized Ising Hamiltonians [8,9] and for nonlinear spherical spin glass models [10].

The issue of the equivalence of statistical ensembles is notably important for one-dimensional systems. In particular, this concept plays a crucial role in the theory of single polymer chains [11–14]. In this case, the deviation of the behavior corresponding to different statistical ensembles is indeed easily observable at both theoretical and experimental level (for chains with a finite number N of domains). In other words, short chains exhibit different physical responses (i.e. constitutive equations) when subjected to different boundary conditions (i.e. statistical ensembles). A large spectrum of single molecule manipulation techniques such as atomic force microscopy, optical and magnetic tweezers, have been recently developed and they allow to study these deviations for arbitrarily long molecules, such as DNA or proteins [15–18]. For the case of single polymer chains under stretching (without confinement effects, i.e. free to fluctuate in the whole space), two ensembles are typically considered [1]: the first one is the Gibbs (or isotensional) ensemble characterized by a deterministic force applied to the free end of the chain (being the other end clamped at the origin of the axes); the second one is the Helmholtz (or isometric) ensemble obtained with both the ends of the polymer tethered at two different points of the space. We remark that these two ensembles correspond to a couple of different canonical distributions, obtained with distinct boundary conditions. In this sense, we are dealing with the equivalence characterization between two dual versions of the canonical ensemble. On the one hand, when the thermodynamic limit is not satisfied (small number of monomers), these two situations are not equivalent, leading to different force–displacement curves [19,20]. This fact has been proven for different polymer models in the literature [21–23]. On the other hand, whenever N approaches infinity, it is important to elucidate if the equivalence of ensembles occurs or not.

Earlier investigations concerning the ensembles equivalence for flexible polymers have been performed adopting both theoretical approaches [21,24–31,19,32,33] and computational methodologies [30,34–37]. Typically the problem is studied by comparing force–extension relations [24,30,37], or by considering conjugated partition functions and the corresponding thermodynamic potentials [31,38]. As anticipated, despite several investigations, there is not an overall consensus on this topic. There are some authors that find agreement between averages determined by different ensembles in the thermodynamic limit, [21,25,22,28,31,30,19,33] while others emphasize non-equivalence [24,26,35–37,32] even in the thermodynamic limit. One of the source of the controversy is the following. The force–extension laws for the two ensembles map different quantities: $\langle \vec{f} \rangle$ and $\vec{r}$ for the Helmholtz ensemble and $\langle \vec{r} \rangle$ and $\vec{f}$ for the Gibbs one. Some authors [24,26,37] have introduced different average values. In particular, they considered the force–extension responses $\langle |\vec{f}| \rangle$ versus $|\vec{r}|$ for the Helmholtz case and the curve $\langle |\vec{r}| \rangle$ versus $|\vec{f}|$ for the Gibbs one. These assumptions involved some apparent inequivalences related to the transformation of random variables introduced to determine the average value of the modulus of the vectors $\vec{r}$ and $\vec{f}$ (in general $|\langle \vec{w} \rangle| \neq \langle |\vec{w}| \rangle$ if $\vec{w}$ is a random vector) [19,32,33]. The reader can find a complete discussion about the origin of the contrasts concerning this problem in Ref. [31].

The investigations above dealt with the case of a polymer chain tethered at both ends with different types of boundary conditions (isometric or isotensional). In all cases no confinement effects have been considered. Another class of problems concerns a flexible polymer chain with one end tethered on a flat substrate surface and the other end free to fluctuate. In this system a piston of fixed geometry tries to confine the chain between the substrate and the piston itself, controlling the desorption and the escape transition [39–41]. The piston behavior can be defined to introduce the h-ensemble, where the distance between piston and substrate is directly controlled, and the f-ensemble, where the compression force applied to the cylinder is the independent parameter. In this system, which falls beyond the scope of the present paper, the confinement effects are of crucial importance. It has been proved that the escape transition of a polymer in these conditions exhibits an unusual non-equivalence between the defined statistical ensembles [39–41]. These results have been theoretically proved and confirmed by molecular dynamic simulations. Such an investigation is very important since it proves the possibility to have a real inequivalence between different versions of the canonical distribution in statistical mechanics. Nevertheless, we remark that these findings cannot be compared with the results of the present paper because of the completely different assumptions on the geometry defining the statistical ensembles considered. In fact, as previously declared, in this paper we do not take into consideration any form of confinement of the polymer chain.

In this paper, the equivalence of the Helmholtz and the Gibbs ensembles in the thermodynamic limit is rigorously proved for a specific class of polymer chains defined by the following assumptions that will be always considered throughout all the paper:

- we suppose to study a non-branched single chain without confinements, i.e. freely fluctuating in the whole space;
- the only constraints consist in the punctual boundary conditions defining the Helmholtz and the Gibbs ensembles;
- we consider all polymer models characterized by an arbitrary pairing interaction between adjacent monomers, described by a continuous energy function $V(x)$;
- we always suppose that the integrals defining both Helmholtz and Gibbs partition functions are convergent everywhere.