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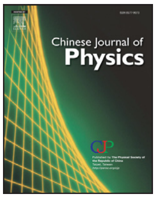

Inequivalence of statistical ensembles in rod-like chains on a one-dimensional lattice

Denise A. do Nascimento, J. Ricardo de Sousa, Minos A. Neto*,
Maressa C. Ribeiro

Departamento de Física, Universidade Federal do Amazonas, 3000, Japiim, 69077-000, Manaus-AM, Brazil

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ABSTRACT

In this work we study a three-state model which has exact solutions in the microcanonical and grand-canonical ensembles showing an inequivalence of statistical ensembles for small systems. We consider N chains placed on an unidimensional lattice, such that each site may assume one of three-states: empty (state 1), with a single molecule energetically null (state 2), and with a single molecule with energy ε (state 3). Each molecule consists of two monomers connected one to each other by a rod.

1. Introduction

Statistical mechanics allows an understanding of the phenomenology described by thermodynamics from microscopic approaches. Initially designed to explain simple phenomena, such as the behavior of monatomic gases, interacting via short-range potentials, this area of physics has developed rapidly and is currently crucial to understanding complex systems [1].

Throughout history, lattice gas model have been studied in the literature for studies of critical phenomena in condensed matter physics [2], among these models are the adsorption models of diatomic molecules. The behavior of diatomic molecules (dimers) adsorbed on surfaces was considered first time by Fowler and Rushbrooke [3]. In the simplest model of this kind, only excluded volume interactions are taken into account, and the relevant quantity is the entropy of placing dimers (which occupy two first neighboring sites) on lattices, which is a fundamental equation of the system.

For the particular case of full occupancy and two-dimensional lattices, this problem was exactly solved by Kasteleyn, Temperley and Fisher [4], where, more recently, this dimer model has been analyzed the universal finite-size scaling functions with exact non-universal metric factors [5] finite-size corrections and scaling with periodic boundary conditions on a square lattice [6], triangular lattice [7] and checkerboard lattice [8].

However, in order to ensure its wide employability, it is necessary to guarantee the existence of the thermodynamic limit, that is, systems with very large number of particles (in the order of Avogadro's number), so that all mechanical-statistical formulations, given by ensemble theory, are equivalent [9], when we apply different types of statistical ensembles to theoretical models, we obtain the same results for the macroscopic physical quantities calculated.

On the other hand, in cases where the thermodynamic limit does not apply, as occurs with so-called "small systems" [10–12], whose range of interactions equals the size of the system, arises the inequivalence ensemble phenomenon. In this

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* Corresponding author.
E-mail addresses: minos@if.uff.br, minos@pq.cnpq.br (M.A. Neto).

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situation the physical predictions made depend on the statistical formalism adopted, it remains to understand which of the mechanical-statistical approaches is relevant.

The interest in small systems is not limited to physics, but also extends to biology and chemistry, passing from agglomerates [13,14], for thin films [15], magnetic nanoparticles [16,17], nonequilibrium statistical mechanics of classical and quantum systems [18] and the biological molecules of some nanometers [19]. These systems have properties different from those of systems considered of macroscopic size. The phase transitions [10], the thermal conductivity [20], the fluctuations of the thermodynamic variables [21], the heat capacity [22], etc. are all affected by the size of the system.

Currently, with the advancement of technology, nanostructured systems have been created, where you can control the number of particles in a material, and you can even work with less than 100 or 50 particles. To treat these systems, the tools of statistical mechanics have been used, which a priori could not happen due to the thermodynamic limit. Therefore, a detailed study of what happens when we apply tools of statistical mechanics to systems with small particles, verifying if these tools applied to the different statistical ensembles still lead to the same results.

We will consider in this work a three-state unidimensional system with empty sites, energetically null single molecules, and single molecules with energy ε, where it is important to emphasize that the molecules are non-interacting. In Section 2 we present the model and formalisms. The entropic sampling simulations are described in Section 3. The results and discussions are presented in Section 4. Finally, the last section is devoted to ultimate remarks and conclusions.

2. Models and formalism

2.1. Model

In the scope of statistical mechanics, in the microcanonical ensemble, entropy appears as a key concept that connects, through Boltzmann's definition, the microscopic configurations of a system, with its macroscopic behavior. In turn, the thermodynamic limit, applied to systems with many particles $\sim 10^{23}$, that ensures the existence of this micro-macroscopic connection is based on the fundamental concept of extensivity of energy and entropy. However, statistical mechanics is a theory created to explain phenomena considering the thermodynamic limit, that is, applied to systems with many particles.

When counting the number of configurations in the microcanonical formalism, combinatory calculations are used as a tool and expressions that involve factorials naturally appear, where in the limit of thermodynamic, the asymptotic approximation of Stirling is used: $\ln x! \cong x \ln x - x$. However, it is unclear whether this approach works for small systems. Miranda et al. [23], by calculating the thermodynamic properties using the factorial itself and substituting the derivatives by finite differences, have shown that the Stirling approximation is imprecise for systems with $N \sim 100$. In our study, as an alternative to replace the factorial terms we will use the Gamma function [24].

We consider an unidimensional model where each molecule consists of two monomers linked by a rod. The number of rods may vary as $0 \leq N \leq L$, where L is the lattice size. Each site may assume one of three states, namely, an empty site, a molecule energetically null, or a molecule with energy ε. In each case, the energy of the state is therefore 0, 0, and ε, respectively. In addition, in this model there is no interaction between rods, nor between the monomers that form the rods.

The Hamiltonian is written as

$$\mathcal{H} = \varepsilon \sum_{i=1}^{L} \delta_{3,q_i}, \tag{1}$$

where the sum extends over all sites of the lattice and q_i represents the state of the site.

2.2. Microcanonical solution

The ground state consists in the lattice being completely empty or with any number of dimers energetically null, the next energy level corresponds to a single dimer with energy ε and any number of dimers energetically null and so on, until the configuration with maximum energy where each site is occupied by a dimer with energy ε [25].

The microcanonical formulation of the model of dimer chains on an unidimensional lattice with two types of dimers is done as follows. Let N_1, N_2, and N_3 be the fixed numbers of empty sites, dimers with zero energy, and dimers with energy ε, respectively. According to (1), the energy of the system can be written as

$$\mathcal{H} = N_3 \varepsilon, \tag{2}$$

The number of ways one can allocate N_1 empty sites, N_2 dimers of type 1, and N_3 dimers of type 2 on an unidimensional lattice of size L is given by

$$\Omega = \frac{L!}{N_1!N_2!N_3!}. \tag{3}$$

Let $N = N_2 + N_3$ be the total number of dimers and $U = N_3 \varepsilon$ the total energy. We can therefore rewrite the number of configurations (3) as a function of U, N, and L as

$$\Omega(U, N, L) = \frac{L!}{(L-N)!(N-U/\varepsilon)!(U/\varepsilon)!}. \tag{4}$$