Entropy of dimers chains placed on a one-dimensional lattice with q-states

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HIGHLIGHTS

- Polymer model.
- Matrix transfer and Monte Carlo algorithm.
- Entropy of dimers chains with q-states.

ARTICLE INFO

ABSTRACT

We calculate the entropy of a chain of dimers placed on a one-dimensional lattice as a function of the density of monomers. We consider N_p dimer chains with a number of monomers $M = 2$ which may assume q-states (orientations) on the one-dimensional lattice. In this work we treated a simple model which has exact solutions both in the micro-canonical and grand-canonical formalisms. The analytic result in the micro-canonical and grand-canonical ensembles were successfully confirmed by a Monte Carlo algorithm.

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1. Introduction

The study of dimers was established by various techniques of condensed matter physics throughout history. The behavior of diatomic molecules (dimers) adsorbed on surfaces was considered by Fowler and Rushbrooke [1]. 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 [2].

Linear polymers are the simplest physical systems that can be studied in the framework of random walk models. They are long chain-like molecules formed by repetition of a basic unit or segment, where the polymer is *flexible*, i.e., it can assume different geometric configurations [3]. Polymer adsorption on a substrate has received considerable attention, both because of its intrinsic merit as an interesting problem in statistical mechanics [4] and because of its technological importance in the stabilization of colloidal dispersions used in paints, pharmaceuticals and foodstuffs [5].

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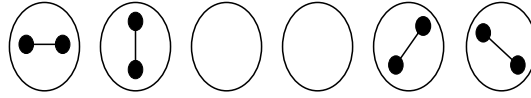 *E-mail address:* minos@pq.cnpq.br (M.A. Neto).

Fig. 1. Section of the lattice with a particular configuration of chains. Here we consider $N_p = 4$ chains with $L = 6$ sites and $q = 4$ states.

Another model of this genre for molecules with multiple adsorption states can be studied using a lattice model [6]. In this kind of model, the statistical thermodynamic functions are used to describe the adsorption of antifreeze proteins onto an ice crystal. Protein adsorption plays an important role due to its possible applications in a variety of technological and biological processes [7–9]. The understanding of the fundamental factors that determine protein adsorption are of importance in developing biosensors, biochip, medical device coating, drugs and the fabrication of novel materials [10–14].

Although Monte Carlo (MC) simulations play an important role for the study of phase transitions and critical phenomena, some well-known difficulties arise when one uses standard algorithms (one-flip algorithms) [15] for the study of random walk models. These difficulties have been overcome by the development of alternative MC methods, such as parallel-tempering [16], cluster algorithms [17], multicanonical algorithms [18], and more recently the Wang–Landau method [19]. This method has been applied with great success to many systems, in particular to polymers in lattice [20–22].

In the present paper, we analyzed a repeated random sampling algorithm to obtain the histogram related to the number of states as a function of the density for a finite linear chain of dimers assuming q-states (orientations), where we compare this simple model (athermal model) with exact solutions in micro-canonical and grand-canonical formalism. Athermal models are those in which all the microscopic configurations allowed have the same energy, which can be assumed to null. More precisely, we may define the entropy of a system of chains with M monomers each placed on a lattice with L sites, as follows

$$s_M(\rho) = \frac{1}{L} \lim_{L \to \infty} \ln \Gamma\left(N_p, M; L\right), \tag{1}$$

where $\Gamma\left(N_p, M; L\right)$ is the number of ways to place N_p chains of dimers ($M = 2$) on the lattice and the thermodynamic limit is taken with fixed density of occupied sites $\rho' = N_p M / L$. Thus, the fundamental equation in the formulation of entropy does not have the energy as a variable, consequently the temperature is not defined, which justifies the name of this category of models.

In this model there is no interaction between chains and nor between the monomers that form the segment (dimers). Initially, the model was described by Ben-Naim [23] for a one-dimensional model with many states (related to the q-state model Potts one-dimensional [24]), which can be adapted to illustrate the hydrophobic effect [25,26]. In Section 2 we present the model and formalisms. The results and discussions are given in Section 3. Finally, the last section is devoted to conclusions.

2. Model and formalisms

2.1. Definition and micro-canonical solution of the q-states model

Let us start with the formulation and micro-canonical solution of the model of dimer chains placed on a one-dimensional lattice with q-states. Fig. 1 shows the schematic picture of the one-dimensional model. We can calculate the number of ways to place N_p chains with each dimers (molecule with a number of monomers $M = 2$) centered at a lattice of $L = Na$ sites in one of q-states (orientations), where a is the lattice parameter that is the distance between two successive sites.

Each circle with a bar represents a dimer of q-state and each open circle is for empty sites. Since in this case there are $L - N_p$ empty sites, it is easy to conclude that this number is equal to

$$\Gamma\left(N_p, M; L\right) = q^{N_p} \frac{L!}{N_p!\left(L - N_p\right)!}. \tag{2}$$

Taking logarithms and applying Stirling's formula, in the thermodynamic limit ($L \to \infty$) we get

$$s = \lim_{L \to \infty} \frac{S}{k_B L} = \rho \ln(q) - \rho \ln(\rho) - (1 - \rho) \ln(1 - \rho), \tag{3}$$

where s is the adimensional entropy per site and $\rho = \rho'/M$ (fraction of occupied sites per dimers $M = 2$).

2.2. Grand-canonical ensemble: transfer matrix technique

In spite of the combinatorial solution, the problem of determining the entropy of dimer chains, with q-states cannot be easily generalized to other lattices, for example two- and three-dimensional lattices. This motivates us to present another way to solve this problem by using the concept of the transfer matrix. Initially, it is necessary to formulate the problem in the grand-canonical ensemble. To define a transfer matrix, we may use lattice gas variables $\delta_i = 0, 1$ associated to the incidence of one dimer in the lattice, such that $\delta_i = 1$, if at least one dimer is between two sites, on the left of the lattice and $\delta_i = 0$, otherwise. In Fig. 2, a possible configuration of the chains is shown.