



Phase diagrams for the adsorption of monomers with non-additive interactions



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ABSTRACT

In several experimental systems phase diagrams coverage-temperature show a strong asymmetry. This behavior can be reproduced by including non-additive lateral interactions. In this work a Monte Carlo study on the canonical assembly of the criticality of monomer adsorption with non-additive interactions is presented. Traditional pairwise energies were replaced by other more general ones where the lateral interaction between two ad-atoms depends on the coverage at first sphere of coordination. This kind of energies includes multibody interactions like three-body interactions and four-body interactions, etc. These energies induce the formation of several non-additive ordered structures. Finite size scaling method was used to classify the order of phase transition of each non-additive phase. On the other hand, the corresponding phase diagrams are formed naturally, in which case the diagrams show strong asymmetries.

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1. Introduction

In surface science the phase diagram of atoms or molecules is one of the most important topics for the characterization of an adsorption system. In the last few years new techniques have improved the perception of the adsorption phenomenon. Nowadays powerful experimental techniques such as LEED and STM [1] allow obtaining much information about topography of surface energy and interactions between particles deposited. Theoretically, a lattice gas model is the simplest tool for calculating phase diagrams. This method immediately induces the conservation of the vacancy-particle symmetry, which means that the diagram coverage-temperature is perfectly symmetric around half coverage when only pairwise interactions are present. However, there are several experimental systems, such as H/Pd(100) [2], H/Ru(001)[3] and Co/Cu(100), where phase diagrams are asymmetric [4]. In fact, adsorption isotherms for methane, ethane, and other adsorbates on AlPO₄-5 and SAPO-5 are clearly unsymmetrical around half coverage [5–9]. The asymmetries have been theoretically studied in general in two ways: by removing the symmetry of the substrate [10] and by introducing multibody interactions like triplets (three-body interactions), and quadruplets (four-body interactions) [11,12]. Within the latter, the authors consider non-pairwise interactions, from which the idea to remove the traditional assumption of additivity arises. Non-additivity means that all lateral energies depend on the quantity of atoms in a cluster.

There are several experimental studies where additivity does not reproduce the main characteristic of the systems. For example, in Ref. [13] the line of coexistence between the condensate phase and the gas phase for Ni, Cu, Pd, and Ag on W(110) shows a strong asymmetry and a strong tendency to dimer formation. Therefore, such additivity does not satisfy these behaviors. The importance of non-additive effects has also been reported in chemisorption and catalysis [14,15]. Other examples where the additive interactions do not complete the description is in the growth of monolayer in heteroepitaxial systems with heterogeneities, such as Ag/Au(100), Ag/Pt(100), Au/Pt(100), Au/Pd(100), Au/Ag(100), Pt/Ag(100), Pt/Au(100) and Pd/Au(100) [16–18]. The formation of the electrochemistry phase in Ag on Au(111) and Au(100) [19–21] needs more complex interactions to be fully understood. Surface restructuring is another example of a system where more complex ad–ad interactions take place [22–25].

In order to explain these behaviors several models have been formulated. Some models include, for example, interactions different from pairwise interactions, or even situations where attractive and repulsive interactions compete [26]. A more complex model has been defined to describe O on W(110). This model includes interactions at nearest, next nearest, nearest-nearest neighbors, and even interactions of three and five particles to obtain an asymmetric phase diagram [27].

The non additive lateral interactions were present in [28,29] for a Grand Canonical Monte Carlo study with attractive interactions. Non-additive interactions were included in theoretical approaches for monomers and dimers [30,31]. In particular, a computational study of adsorption of repulsive monomers with non-additive interactions on square lattice were performed [32]. On the whole, the main results are: i) depending on the values of the non-additivity the $c(2 \times 2)$ ordered

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phase (as compared to the additive case) is weakened or strengthened. It is also possible to notice the presence of different low-temperature ordered phases depending on the surface coverage. These findings are corroborated by very wide plateaus in the adsorption isotherms, steps in the isosteric heat and weak peaks in the thermodynamic factor. ii) The formation of k -mers is corroborated in a specific range of coverage and interactions. iii) There is evidence of a continuous phase transition from the $c(2 \times 2)$ structure to disorders around to half coverage for non-additive schemes. Similar results have been found in studies on the thermodynamics of adsorption on triangular and hexagonal lattices [33] and nanotube bundles [34].

For the purpose of clarity, Fig. 1 shows the snapshots of three structures formed at several surface coverages (θ), specifically at $\theta = 1/2$, the well-known $c(2 \times 2)$, at $\theta = 2/3$ and $\theta = 4/5$ the dimeric and tetrameric phase respectively. The last two are new structures induced by non-additivity. This paper aims at exploring how non-additivity affects the phase diagram and the critical exponents. Consequently, Monte Carlo simulations in the canonical assembly and finite-size scaling for each phase founded in square lattices are used.

The paper is organized as follows: In Section 2, the non-additive model is presented. In Section 3, details of Monte Carlo Simulations and finite size scaling theory are given. Results and discussion of the criticality and phase diagrams are presented in Section 4. Finally, the conclusions are drawn in Section 5.

2. The theoretical model

An idealized solid surface with a square geometry of linear dimension L was considered for the analysis. A lattice-gas model with $N = L \times L$ specific adsorption sites was used. For this geometry each site has four nearest neighbors separated by a lattice constant. In order to consider the simplest possible model for non-additive ad-ad particles, a homogeneous potential surface “as seen” by an adsorbed particle shall be considered. Two kinds of energies can be taken into account, the adsorbate–substrate energy ε , and lateral interaction between i and j particles, as w_{ij} . To be more specific, a Hamiltonian can be defined as:

$$H = -\varepsilon \sum_{i=0}^N c_i + \sum_{i \neq j}^N w_{ij} c_i c_j \quad (1)$$

where the local occupation variable c_i is 0 (1) if the adsorption site is empty (occupied). ε is independent of the temperature and coverage and can be considered equal to zero without losing generality. So as to include the non-additivity, we considered that w_{ij} depends on the

occupation state of both sites i and j . The real dependence of w_{ij} on the local coverage is difficult to establish by means of an experiment. The aim of this contribution is to explore a case where the main features of the presence of non-additive interactions are kept. In order to draw general conclusions on how such interactions affect the critical behavior of thermodynamic quantities we assume that each ad-particle has four different possible configurations depending on the number of the nearest neighbors. Then, the energies are w_1, w_2, w_3 and w_4 . The lateral energy between two particles is considered to be an average of the energies of their respective environments. Fig. 2 shows an example for calculating the lateral energy between the particles 1 and 4. The multibody interactions such as triplets and quadruplet are included in the modeling as shown in Fig. 2. The real function or rule that links each energy with the number of the nearest neighbors “ m ” on the vicinity of adatoms is not clear. But several clues indicate that this relation could be linear. Among them, Koh and Ehrlich [35] found, by using the helium-cooled field ion microscopy technique, that the pair free energies of Pd and Ir clusters on W(110) are linear with the size. Then, it is physically reasonable to suppose that the lateral interactions depend linearly on the number of the nearest neighbors “ m ” on the vicinity of a given atom. So, in this model, w_m varies linearly with m and $w_z = w$, where z is the coordination number of the lattice. Following Ref. [28] we introduce the parameter of non-additivity, $P = w_1/w_2$ as a measure of the strongest to the weakest possible bonds in the system, then:

$$\frac{w_m}{w} = \frac{Pz-1}{z-1} - m \frac{P-1}{z-1}. \quad (2)$$

This situation has been tackled by Mean Field Approach (MFA) [25] and Quasi-Chemical approach (QCA) [28,30,31]. However, the analysis given in the cited papers has been restricted to some especial cases mainly including attractive interactions. The discussion presented in the present paper covers the entire range of repulsive interactions, temperatures and coverage.

As mentioned at the beginning of this section, the present study was restricted to the case of homogeneous surfaces. More complex adsorbents (including energetic and geometric heterogeneity, surface reconstruction, anisotropy, etc.) could be treated by using a similar scheme as discussed here. Under these conditions, it is expected that the presence of a very small quantity of defects breaks down the order of the low-temperature phases. However, even though the presence of defects affects the formation of ordered structures in the adlayer, it is also expected that the phase transition survives up to a certain critical degree of disorder [36,37].

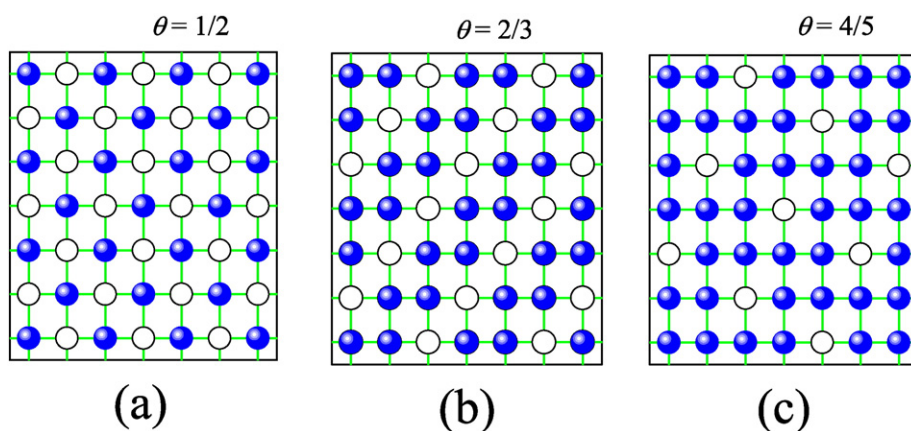


Fig. 1. Snapshot of non-additive structures. White circles correspond to empty sites and the blue ones to filled sites. A) $c(2 \times 2)$ structures, b) dimeric phase, and c) tetrameric phase. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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