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Reversible adsorption on a random site surface

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Abstract

We examine the reversible adsorption of hard spheres on a random site surface in which the adsorption sites are uniformly and randomly distributed on a plane. Each site can be occupied by one solute provided that the nearest occupied site is at least one diameter away. We use a numerical method to obtain the adsorption isotherm, i.e. the number of adsorbed particles as a function of the bulk activity. The maximum coverage is obtained in the limit of infinite activity and is known exactly in the limits of low and high site density. An approximate theory for the adsorption isotherms, valid at low site density, is developed by using a cluster expansion of the grand canonical partition function. This requires as input the number of clusters of adsorption sites of a given size. The theory is accurate for the entire range of activity as long as the site density is less than about 0.3 sites per particle area. We also discuss a connection between this model and the vertex cover problem.

Keywords: Adsorption; Random site surface; Cluster expansion; Vertex cover

1. Introduction

The adsorption of proteins and colloids at a liquid–solid interface is a key step in many natural and industrial processes such as filtration, chromatography, protein purification, immunological assays, biosensors, biomineralization and biofouling. In many of these situations, the surface of the adsorbent is heterogeneous. For example, in immunological assays one typically employs colloidal particles that have been coated with proteins (antibodies) to bind with antigens that may be present in the sample. Similarly, in affinity chromatography, the adsorbent is synthesized by immobilizing certain affinity ligands on porous silica, agarose or synthetic polymers. Many of these applications can benefit from a quantitative knowledge of the amount of solute that is adsorbed as a function of the bulk concentration, ligand density and distribution and solute properties such as the size.

The modeling approach required depends on the nature of the adsorption. When there is a finite desorption probability, characterized by a non-zero desorption rate constant, an equilibrium between the bulk and adsorbed phases will be established; rapidly if the desorption rate is large and more slowly for small desorption rates. The properties of the equilibrium state, in particular the adsorption isotherm, depend on the bulk phase

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activity. If the desorption rate constant is very small on the experimental time scale the adsorption is effectively irreversible and a different approach is required.

The statistical mechanics of reversible adsorption on heterogeneous surfaces, particularly for gases on solids, has a long history. Pioneering work was performed by Hill [1] and Steele [2] and it is still an active area of research [3,4]. There is also a well-developed literature on irreversible adsorption on homogeneous surfaces [5–7]. Some models specifically address irreversible adsorption on non-uniform surfaces [8–11] where macromolecules are represented as hard spheres that bind irreversibly to adsorption sites. In the simplest of these, the random site surface (RSS) [8], the sites are represented by randomly distributed points. Adamczyk et al. [10] extended the basic model to the situation where the adsorption sites have finite dimensions. The adsorption of colloidal [12,13] and nanoparticles [14] has been interpreted with these models and a similar hard sphere model was used to rationalize the adsorption of proteins to hydrophobic sites on mixed self-assembled monolayers [15].

Although macromolecules such as colloids and proteins have a tendency to adsorb irreversibly, this is not always the case and it is certainly useful to understand the equilibrium behavior. In this article we therefore present numerical and approximate analytical results for reversible adsorption of hard spheres on the RSS. For irreversible adsorption on this surface the task of developing a theoretical description was greatly simplified by the existence of an exact mapping to an analogous process on a continuous (homogeneous) surface [8]. For reversible adsorption on the RSS surface, however, there appears to be no similar mapping that would allow us to exploit the known behavior of hard spheres on continuous surfaces [16,17].

In addition to its application to adsorption, the RSS model is also interesting from another perspective. Weight and Hartmann obtained analytical results for the minimal vertex cover on a random graph by a mapping to a hard sphere lattice gas [18,19]. A vertex cover of an undirected graph is a subset of the vertices of the graph that contains at least one of the two endpoints of each edge. In the vertex cover problem one seeks the *minimal vertex cover* or the vertex cover of minimum size of the graph. This is an NP-complete problem meaning that it is unlikely that there is an efficient algorithm to solve it.

The connection to the adsorption model is made by associating a vertex with each adsorption site. An edge is present between any two vertices (or sites) if they are closer than the adsorbing particle diameter. The minimal vertex cover corresponds to densest particle packings. Weight and Hartmann obtained an analytical solution for the densest packing of hard spheres on random graph using a replica-symmetric approach. Although the random graph is related to the RSS model, it is not the same as the former does not have a physical structure. Specifically, in a random graph each possible edge is present with a given probability, c. In the random site surface, on the other hand, two adsorption sites that are neighbors of a given site are more likely to be neighbors of each other than two randomly selected sites. This effect can be quantified by the clustering coefficient, which is the average probability that two neighbors of a given vertex are also neighbors of one another.

In Section 2 we define the model and the simulation procedure. Section 3 compares numerical results for the maximum coverage with various theoretical estimates. The structure of the random site surface is discussed in Section 4, and Section 5 presents an approximate theory for the adsorption isotherms that applies at low adsorption site density.

2. Model and simulation

The adsorbent surface consists of N_s point sites that have been uniformly and randomly distributed on a surface of area L^2. These sites are frozen in place. The adsorbate molecules are represented by hard spheres of diameter σ. In order to adsorb, a hard sphere must bind, centered, to one site. An adsorbed sphere may cover any number of sites but only occupies (or interacts with) the one at its center. Any site that lies within a distance σ of an occupied site is unavailable. See Fig. 1. It is convenient to introduce a dimensionless site density

$$\alpha = \frac{\pi\sigma^2 N_s}{4L^2} \tag{1}$$