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A cluster-exact approximation study of the adsorption of binary mixtures on heterogeneous surfaces

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ABSTRACT

The adsorption of binary mixtures on heterogeneous surfaces is studied by a cluster approximation (CA), based on the exact calculation of configurations on finite cells. The substrate is characterized by n types of sites, each with different adsorption energy. The process is monitored through the total and partial isotherms. The theoretical formalism is used to model experimental data of methane–ethane mixtures adsorbed on a template-synthesized carbon. The CA results are compared with the ones corresponding to the well-known Ideal Adsorbed Solution Theory (IAST). Even though a good fitting is obtained from IAST, it is found that CA is a more accurate model to estimate the binary data on the highly heterogeneous carbon sample.

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1. Introduction

Physical adsorption is one of the basic mechanisms that are present in many molecular processes of great technological interest (catalysis, corrosion, lubrication, detergency, etc.) [1–3]. This fact, along with the intrinsic heterogeneity characterizing the real adsorbents, makes the study of adsorption on heterogeneous surfaces especially interesting and one of the most important topics of physical chemistry of surfaces [4,5].

For adsorption of single species, a seminal contribution was made by Langmuir, who derived the monolayer adsorption isotherm for a monoatomic molecule gas adsorbed on a homogeneous surface, without lateral interactions among the adsorbed molecules [6]. Later, some theories were proposed to describe multilayer adsorption [7–17]. Among them, the conventional Brunauer–Emmett–Teller (BET) [7], Guggenheim–Anderson–de Boer (GAB) [8–10] and Frenkel–Halsey–Hill [11–13] models are the simplest and provide the basis to construct more elaborate approaches. These models have played an important role in the characterization of solid surfaces by means of gas adsorption.

More recently, Dutcher et al. [18] extended the BET and GAB models to include arbitrary numbers of additional adsorbed monolayers. Using statistical mechanics, the authors derived expressions for solute and solvent activities in single-solute solutions. In Ref. [19], the model was generalized for mixtures containing an arbitrary number of solutes. The theoretical results were applied to study osmotic coefficients and water activities of aqueous solutions.

In the case of adsorption of multicomponent gas mixtures, the problem is more demanding from a theoretical and experimental point of view [20,21]. For pure components, the number of adsorbed molecules can be accurately determined by simply measuring the weight increase of the adsorbent sample, for mixtures one has to carry out additional experiments to determine the composition in the sample. Thus, although this problem has been studied for decades [20–32], there are many aspects which are not yet completely solved. In fact, most of the studies are devoted to the adsorption of mixtures on homogeneous surfaces. On the other hand, if some sort of surface heterogeneity exists, the statistical problem becomes exceedingly difficult.

However, several attempts were done in the past in order to solve the problem of mixture adsorption on heterogeneous adsorbents. A seminal contribution to this field was done by Sircar [33–35], who developed a model, called heterogeneous Langmuir (HL) model, capable of describing the effect of surface heterogeneity on pure and multicomponent adsorption. HL model is based on two main assumptions: (1) the adsorbent can be described by a patchwise distribution of Langmuirian sites, and (2) a uniform distribution of Henry's law constants characterizes the energetic heterogeneity. Beyond this important theoretical contribution, the description of the process of adsorption in the presence of multicomponent adsorbates and heterogeneous surfaces is a complex problem that does not have yet an exact statistical mechanical treatment.

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One way of overcoming these experimental and theoretical complications is to develop simplified models. In this line, a cluster-exact approximation (CA) was presented in a recent paper from our group [36]. This theoretical approach, based on the exact calculation of configurations on finite cells, is a brute force approximation to the system partition function [37,38].

In our previous work [36], CA proved to be a very useful tool for the research of adsorption of binary mixtures on homogeneous surfaces. The results showed, in addition, that CA could be applied to model experimental data of multicomponent adsorption.[1] Here, the scheme introduced in Ref. [36] is extended to include non-regular surfaces. For this purpose, a cluster composed by m sites of n different types (heterogeneous substrate) is used to calculate the partition function of the system. In this framework, partial and total adsorption isotherms are obtained in terms of the adsorbate–substrate adsorption energies. These energies are determined by adjusting the pure component adsorption data with a weighted sum of homogeneous adsorption isotherms (each homogeneous isotherm represents the adsorption on a type of lattice site).

The theoretical scheme is applied to model experimental data of methane–ethane mixtures adsorbed on a template-synthesized carbon [39]. In addition, experimental and CA results are compared with the classical Ideal Absorbed Solution Theory (IAST) [40]. IAST has become the benchmark for studying adsorption equilibrium of gas mixtures from the isotherms of the pure components. This theory (1) is a predictive model which does not require the gas mixture data; (2) is independent of the model of physical adsorption; and (3) provides a powerful tool to compare the predictions from different adsorption models [33–35,39,41–43].

The paper is organized as follows. In Section 2, the cluster approximation for binary mixtures adsorbed on heterogeneous surfaces is developed. In order to test the applicability of the proposed model, Section 3 is devoted to (1) the analysis of experimental data for methane–ethane mixtures adsorbed on a template-synthesized carbon, and (2) the comparison with results obtained from the well-known IAST. Finally, the conclusions are drawn in Section 4.

2. Theory: cluster-exact approximation for binary mixtures adsorbed on heterogeneous surfaces

The heterogeneous surface is represented by a lattice with M_1, $M_2, \ldots, M_n$ adsorption sites of kind $1, 2, \ldots, n$, respectively. The total number of lattice sites M results:

$$M = \sum_{j=1}^{n} M_j. \tag{1}$$

To describe a system consisting of N adsorbed molecules ($N = N_a + N_b$, being $N_a[N_b]$ the number of molecules of $a[b]$ species) on a lattice of M sites at a given temperature T, the occupation variable σ_i is introduced: $\sigma_i = 0$ if site i is empty, and $\sigma_i = 1[2]$ if site i is occupied by an $a[b]$ particle. Then, in the grand canonical ensemble, the model is characterized by the Hamiltonian:

$$H = \frac{1}{2}\sum_{i}^{M}\sum_{l(i)} \left[w_{aa}\delta_{\sigma_i,\sigma_l,1} + w_{bb}\delta_{\sigma_i,\sigma_l,2} + w_{ab}\left(\delta_{\sigma_i,1}\delta_{\sigma_l,2} + \delta_{\sigma_i,2}\delta_{\sigma_l,1}\right)\right] + \sum_{i}^{M}\left[\epsilon_{a,i}\delta_{\sigma_i,1} + \epsilon_{b,i}\delta_{\sigma_i,2}\right] - \sum_{i}^{M}\left[\mu_a\delta_{\sigma_i,1} + \mu_b\delta_{\sigma_i,2}\right], \tag{2}$$

[1] CA could also be applied to systems of multisolute solutions, as those studied in Refs. [18,19].

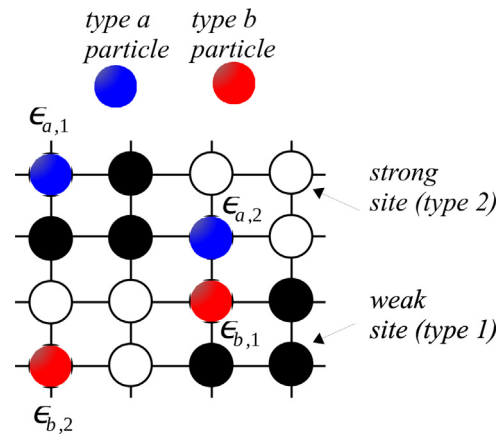

Fig. 1. Cartoon representing a cluster of size $m = 16$ with two different kinds of sites ($n = 2$), $m_1 = 8$ and $m_2 = 8$. In the figure, strong (open circles) and weak (solid circles) sites are arranged in a chessboard structure. Blue [red] circles correspond to $a[b]$ particles. (For interpretation of reference to color in this figure legend, the reader is referred to the web version of this article.)

where the summation over $l(i)$ represents a sum running over the all the nearest-neighbor sites of i; the pairwise interactions, w_{aa}, w_{ab}, w_{bb} are assumed to occur between nearest neighbors only; the symbol δ represent the Kronecker delta; and μ_a, μ_b are the chemical potentials of both species. $\epsilon_{a[b],i}$ denotes the interaction energy corresponding to a molecule of the $a[b]$ species adsorbed on the site i. Then, $\epsilon_{a[b],i}$ can take n values $\{\epsilon_{a[b],1}, \epsilon_{a[b],2}, \ldots, \epsilon_{a[b],n}\}$ according to the type of the site i.

In the context of the lattice-gas approximation, the state of the system is characterized only by the occupation numbers (σ_i with $i \in 1, 2, \ldots, M$). To calculate the coverage of each system state and the thermodynamic quantities of the system, a cluster approximation has been developed. The cluster consists of m ($m \ll M$) sites, arranged in a given geometry, and forming a sub-system with $m_1, m_2, \ldots, m_n$ adsorption sites of kind $1, 2, \ldots, n$, respectively ($m = \sum_{j=1}^{n} m_j$). In the calculations, periodic boundary conditions are considered. As an example, Fig. 1 shows a cluster of size $m = 16$ with two different kinds of sites ($n = 2$), $m_1 = 8$ and $m_2 = 8$. In the figure, strong (open circles) and weak (solid circles) sites are arranged in a chessboard structure.

The exact grand partition function for the cluster can be written as follows:

$$\Xi = 1 + \sum_{\substack{N_a, N_b = 0 \\ 1 \le N_a + N_b \le m}}^{m} \lambda_a^{N_a}\lambda_b^{N_b}\left\{\sum_{E} g(E, N_a, N_b)\exp\left(-E/k_BT\right)\right\}, \tag{3}$$

where k_B is the Boltzmann constant and $\lambda_a \equiv \exp(\mu_a/k_BT)[\lambda_b \equiv \exp(\mu_b/k_BT)]$ is the activity of the $a[b]$ species. $g(E, N_a, N_b)$ is the number of configurations corresponding to N_a adsorbed a-particles and N_b adsorbed b-particles having the same energy E, being

$$E = w_{aa}N_{aa} + w_{ab}N_{ab} + w_{bb}N_{bb} + \sum_{j=1}^{n}\left(N_{a,j}\epsilon_{a,j} + N_{b,j}\epsilon_{b,j}\right), \tag{4}$$

where N_{aa}, N_{ab} and N_{bb} represent the number of aa, ab and bb pairs, respectively, on the cluster; and $N_{a[b]j}$ denotes the number of $a[b]$ particles adsorbed on sites type j.

The partial adsorption isotherm corresponding to the $a[b]$ species can be obtained from Eq. (3) [44],

$$\theta_{a[b]} = \frac{k_BT}{m}\left(\frac{\partial \ln \Xi}{\partial \mu_{a[b]}}\right)_{T,\mu_{b[a]}}. \tag{5}$$

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