Monte Carlo study of binary mixtures adsorbed on square lattices

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ABSTRACT

The monolayer adsorption of interacting binary mixtures on 2D square lattices has been studied through grand canonical Monte Carlo simulation in the framework of the lattice-gas model. The process has been monitored through total and partial isotherms and differential heats of adsorption corresponding to both species of the mixture. Repulsive lateral interactions between the adsorbed particles have been considered, resulting in a rich variety of structural orderings in the adlayer. At the end of this work, the phase diagram characterizing the transitions occurring in the system has been determined. A nontrivial interdependence between the partial surface coverage of both species was observed and discussed.

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1. Introduction

Adsorption of gas mixtures on solid surfaces is a process of fundamental interest for various technological applications, especially gas separation and purification [1–4]. Although this topic has been theoretically [5–12] and experimentally [11–15] studied for decades, many aspects of the problem remain unexplored.

As in any adsorption process, a complete analysis of the behavior of gas molecules under the influence of an adsorbent requires the knowledge of the forces of molecular interactions [1,16–18]. In other words, the description of real single or multicomponent adsorption requires to take into account the effect of the lateral interactions between each species of the mixture. An exact treatment of this problem, including adsorbate–adsorbate interactions, is unfortunately not yet available and, therefore, the theoretical description of adsorption relies on simplified models [4]. In this framework, a valuable contribution has been made by the group of Y. K. Tovbin, who studied pure and mixed adsorption in the presence of lateral interactions and surface heterogeneity [19–22]. On the basis of a new theoretical method (so-called fragment cluster method) and by using different approximations in the context of the lattice-gas theory, the authors investigated the effects of the phase transitions occurring in the system on the main properties of adsorption (isotherm and heat of adsorption).

Adsorption of mixtures is also a much demanding problem from the experimental point of view. Whereas for pure components the number of adsorbed molecules can be determined accurately 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. This is one of the reasons for the lack of polyatomic mixture adsorption data.

One way of overcoming these experimental and theoretical complications is to use Monte Carlo (MC) simulation method [23–27]. MC technique is a valuable tool for studying surface molecular processes, which has been extensively used to simulate many surface phenomena including adsorption [28], diffusion [29], reactions, phase transitions [30], etc. Here we will try to demonstrate that numerical simulations, combined with a correct theoretical interpretation of the results, can be very useful to obtain a very reasonable description of the adsorption of interacting binary mixtures on 2D square lattices.

In this line of work, a previous article was devoted to the study of the adsorption of mixtures of two species on triangular lattices [31]. In Ref. [31], Rinaldi et al. obtained adsorption isotherms and differential heats of adsorption corresponding to both species of the mixture, for different values of the lateral interactions between the adsorbed species. An unusual feature [1] was observed when (i) the lateral interaction between A and B particles was different from zero, and (ii) the initial concentration of B particles was in the range [0.3, 0.5]. In these conditions, the A particles adsorbing on the lattice expel the B adsorbed particles; then, the partial A [B] coverage increases [decreases]. During this regime the number of desorbed particles is greater than the number of adsorbed particles which results in a decreasing of the total coverage that occurs for a wide range in values

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[1] By using quasi-chemical approach and fragment cluster method, this unusual behavior was previously studied by Y. K. Tovbin for adsorption of pure components on heterogeneous surfaces [19,20].

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of chemical potential where the slope of the adsorption isotherm is negative. The behavior of the system was fully explained through the analysis of the phase diagrams for order–disorder transitions occurring in the adsorbed layer.

Because the structure of lattice space plays a fundamental role in determining the statistics of mixtures, it is of interest and of value to inquire how a specific lattice structure influences the main thermodynamic properties of adsorbed mixtures. In this context, the objectives of the present paper are (1) to extend the previous work to square lattices using the same techniques developed in Ref. [31] and (2) to study the effect of the lattice structure on the adsorption of interacting binary mixtures. For this purpose, bicomponent gases adsorbed on square lattices are studied by using grand canonical ensemble MC simulation. Special interest is devoted to the repulsive case, where different ordered structures in the adsorbate are observed for low temperatures.

The model considered here is a particular case of the Blume–Emery–Griffiths model [32] (or its equivalent belonging to the family of q-state Potts models [33]), which is a very general model, used in a variety of phenomena ranging from liquid helium phase separation to phase transitions in adsorbed films [32,34–39]. In the present study, the detailed behavior of adsorption isotherms and heats of adsorption will be shown to be directly related to the phase diagrams of the system.

2. Lattice-gas model and Monte Carlo simulations

The adsorptive surface is represented by a two-dimensional square lattice of $M = L \times L$ adsorption sites, with periodic boundary conditions. The substrate is exposed, at a temperature T, to an ideal gas phase consisting of a binary mixture of particles A and B with chemical potentials μ_A and μ_B, respectively. Particles can be adsorbed on the lattice with the restriction of at most one adsorbed particle per site and we consider a nearest-neighbor (NN) interaction energy w_{XY} (X, Y = A, B) among them. The adsorbed phase is then characterized by the Hamiltonian:

$$H = \frac{1}{2}\sum_{i}^{M}\sum_{l\in\{NN,i\}}\left[w_{AA}\delta_{c_i,c_l,1} + w_{BB}\delta_{c_i,c_l,-1} + w_{AB}\left(\delta_{c_i,1}\delta_{c_l,-1} + \delta_{c_i,-1}\delta_{c_l,1}\right)\right]$$
$$+ \epsilon_0\sum_{i}^{M}\left(\delta_{c_i,1} + \delta_{c_i,-1}\right) - \sum_{i}^{M}\left(\mu_A\delta_{c_i,1} + \mu_B\delta_{c_i,-1}\right)$$

(1)

where c_i is the occupation number of site i ($c_i = 0$ if empty; $c_i = 1$ if occupied by A and $c_i = -1$ if occupied by B); $l \in \{NN,i\}$ runs on the four NN sites of site i; the δs are Kronecker delta functions and ε_0 is the interaction energy between a monomer (type A or B) and a lattice site. In this contribution, the chemical potential of one of the components is fixed throughout the process ($\mu_B = 0$), while the other one (μ_A) is variable, as it is usually assumed in studies of adsorption of gas mixtures [19,21,22]. In the actual implementation of the model ε_0 was set equal to zero, without loss of any generality.

The adsorption process is simulated through a grand canonical ensemble Monte Carlo method [28]. For a given value of the temperature T and chemical potentials μ_A and μ_B, an initial configuration of A and B particles adsorbed at random positions is generated. Then an adsorption–desorption process is started, where a site is chosen at random and an attempt is made to change its occupancy state with probability given by the Metropolis rule [40]

$$P = \min\{1, \exp(-\Delta H/k_B T)\},$$

(2)

where $\Delta H = H_f - H_i$ is the difference between the Hamiltonians of the final and initial states and k_B is the Boltzmann constant. A Monte Carlo step (MCS) is achieved when M sites have been tested to change its occupancy state.[2] The approximation to thermodynamical

equilibrium is monitored through the fluctuations in the number of adsorbed particles; this is usually reached in 10^6 MCS. After that, mean values of thermodynamic quantities, like total and partial isotherms are obtained as simple averages over m successive configurations:

$$\theta(\mu_A,\mu_B) = \frac{\langle N \rangle}{L^2} \quad \theta_A(\mu_A,\mu_B) = \frac{\langle N_A \rangle}{L^2} \quad \theta_B(\mu_A,\mu_B) = \frac{\langle N_B \rangle}{L^2}$$

(3)

where the brackets mean the time average over the m Monte Carlo simulation runs (in our calculations we have used $m = 10^6$). $N_A(N_B)$ and N denote the number of adsorbed A(B) molecules and the total number of adsorbed particles, respectively. Accordingly, $\theta_A(\theta_B)$ and θ represent the partial surface coverage of the A(B)-species and the total surface coverage, respectively.

The differential heat of adsorption q_i for the i-specie is defined as [41–43]:

$$q_i = -\left(\frac{\partial U}{\partial N_i}\right)_{T,N_{j\neq i}}$$

(4)

where U is the energy of the adsorbed phase. Using basic relationships from the thermodynamics of adsorption and expressing the derivatives as fluctuations in the grand canonical ensemble, the following forms for the differential heats of adsorption can be obtained [27,31]:

$$q_A = -\frac{\Phi(A)\left[\langle N_B^2 \rangle - \langle N_B \rangle^2\right] - \Phi(B)[\langle N_A N_B \rangle - \langle N_A \rangle\langle N_B \rangle]}{\left[\langle N_A^2 \rangle - \langle N_A \rangle^2\right]\left[\langle N_B^2 \rangle - \langle N_B \rangle^2\right] - [\langle N_A N_B \rangle - \langle N_A \rangle\langle N_B \rangle]^2}$$

(5)

$$q_B = -\frac{\Phi(B)\left[\langle N_A^2 \rangle - \langle N_A \rangle^2\right] - \Phi(A)[\langle N_A N_B \rangle - \langle N_A \rangle\langle N_B \rangle]}{\left[\langle N_A^2 \rangle - \langle N_A \rangle^2\right]\left[\langle N_B^2 \rangle - \langle N_B \rangle^2\right] - [\langle N_A N_B \rangle - \langle N_A \rangle\langle N_B \rangle]^2}$$

(6)

where

$$\Phi(\alpha) = \langle U N_\alpha \rangle - \langle U \rangle\langle N_\alpha \rangle.$$

(7)

3. Results and discussion

The study has been focused on the case of repulsive lateral interactions among adsorbed particles since, as it will be seen, different structures appear in the adsorbed phase. The computational simulations have been developed for square $L \times L$ lattices with $L = 96$ and periodic boundary conditions. The finite-size effects on the adsorption properties were investigated by considering systems of increasing sizes (ranging between $L = 6$ and $L = 120$). As an example of such studies, Fig. 1 shows, for a typical case ($w_{AA}/k_B T = 4$, $w_{BB}/k_B T = w_{AB}/k_B T = 0$, $\mu_A/k_B T = 2$ and $\mu_B/k_B T = 0$), how the equilibrium surface coverage varies with the lattice size. As it can be observed, finite-size effects are negligible for $L > 48$. Note, in addition, that the linear dimension L has to be properly chosen such that the adlayer structure is not perturbed.

3.1. Adsorption results

In order to understand the basic phenomenology, the case of single-gas adsorption was considered in the first place. This was achieved by making $\mu_B \rightarrow -\infty$. Fig. 2 shows the behavior of the adsorption isotherms for different strengths of repulsive interparticle interactions. As expected, the well-known Langmuir isotherm, passing through the point ($\mu_A/k_B T = 0$, $\theta_A = 1/2$), was obtained for $w_{AA}/k_B T = 0$. Two features, which are useful for the analysis of mixed-gas adsorption, are worthy of comment: (a) as the NN repulsive interaction is increased, the coverage at zero chemical potential decreases and asymptotically approaches $\theta_A \approx 0.226$; (b) as the repulsive NN interaction passes a critical value

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[2] Interested readers are referred to Ref. [31] for a more complete description of the algorithm to carry out an elementary MCS.