

## Surface diffusion in the framework of lattice gas model: mean field treatment and Monte-Carlo method

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We have studied the lattice gas model subject to nearest neighbour repulsive interactions with the Monte-Carlo method leading to a clear understanding of order-disorder transition and its effect on the adsorption and intercalation processes. The lattice division into two (three) sublattices in the case of the square (triangular) lattice enables us to underline the appearance and the growth of the ordered phase. A comparison between the mean field approximation and Monte-Carlo results is also presented.

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### I- INTRODUCTION

Recently there has been a vivid interest in the modelling of chemisorbed or physisorbed monolayers at surfaces in terms of lattice gas models [1,2]. By these models, order-disorder phenomena in the monolayers can be interpreted in terms of powerful tools of the modern theories about critical phenomena [3-5]. While in previous work most emphasis has been on static properties of the model, such as the phase diagram, adsorption isotherms, order parameters, ordering energies, etc., relatively little attention has been paid to the dynamics of such systems. Clearly, a better understanding of surface diffusion at arbitrary coverage may be an important ingredient of theoretical analysis of complicated processes at surfaces such as catalysis, corrosion, etc....

In the present paper, we study surface diffusion in the framework of lattice gas model, where the adatoms can occupy only preferred sites of a lattice determined by the substrate surface. We study the effect of lateral interactions on surface diffusion by the Monte-Carlo simulation for a broad reduced interaction.

The outline of our paper is as follows. In section 2, we briefly define the quantities of interest for general lattice gas models, we summarize the relevant static properties of our square (triangular) lattice gas model and we also discuss the mean field approach results. In section 3 we introduce the Monte Carlo method and we present our simulation results for different choices of interaction parameter, while section 4 contains our conclusions.

### II- GENERAL THEORY

#### A- Lattice gas model

In the lattice gas, a local occupation variable  $n_i$  is associated with each lattice site, where  $n_i=1$  if the

lattice site  $i$  is occupied by a particle, while  $n_i=0$  otherwise.

Assuming pair interaction between particles, the hamiltonian  $H$  of the lattice gas takes its usual form as an expansion in terms of the  $\{n_i\}$ .

$$H = -\frac{1}{2} \sum_{ij} \epsilon_{ij} n_i n_j - \mu \sum_i n_i \quad (1)$$

where  $\epsilon_{ij}$  are the pairwise interaction parameters and  $\mu$  is the chemical potential [6].

The configuration  $\{n\}$  represents the set of occupation numbers for each site that we note for a lattice with  $N$  sites.

$$\{n\} = \{n_1, n_2, \dots, n_N\}$$

The diffusion process of the particles is assured by the change of the occupation numbers of the lattice sites. In the lattice gas formulation this can be seen as the change of the lattice configurations. The dynamic of the lattice is then governed by the phenomenological master equation [6], which describes the evolution in time of the probability  $P(\{n\}, t)$  of the configuration  $\{n\}$ .

$$\frac{\partial P(\{n\}, t)}{\partial t} = \sum_{\{n'\}} \omega(\{n'\}, \{n\}) P(\{n'\}, t) - \omega(\{n\}, \{n'\}) P(\{n\}, t) \quad (2)$$

The rate of the configurations exchange is expressed by the transition frequency  $\omega(\{n'\}, \{n\})$  which encloses all physical information of the considered system. The transition frequency is supposed to satisfy the detailed balance condition that insures the equivalence of transitions between the system equilibrium states:

$$\omega(\{n\}, \{n'\})P_{eq}(\{n\}) = \omega(\{n'\}, \{n\})P_{eq}(\{n'\}) \quad (3)$$

The choice of an analytic expression for the transition frequency is determinant for the investigation of the expected behaviour [8]. In our case, we restrict the jumps of the mobile particles between nearest-neighboring sites only, hence, the transition frequency has the same form as in ref. [7].

The average concentration over all possible configurations is defined by :

$$p(i) = \langle n_i \rangle = \sum_{\{n\}} n_i P(\{n\}, t) \quad (4)$$

Its time evolution is given by the following master equation: (5)

$$\frac{\partial p(i)}{\partial t} = \sum_a w_{i \rightarrow j}(\{n\}) n_j (1 - n_i) - w_{i \rightarrow j}(\{n\}) n_i (1 - n_j)$$

where  $w_{i \rightarrow j}(\{n\})$  is the jump probability operator.

This equation introduces a current operator  $J_{i,j}(\{n\})$

along the bond  $i \rightarrow j$ , considering the symmetric properties of the lattice, eq. (5) takes the form :

$$\frac{\partial p(i)}{\partial t} = -\frac{1}{2} \sum_a J_{i,j}(i) - J_{j,i}(i+a)$$

with

$$J_{i,j}(\{n\}) = w(\{n\}, i, a) n_i (1 - n_j) - w(\{n\}, j, -a) n_j (1 - n_i)$$

The jump probabilities  $w_{i \rightarrow j}(\{n\}) = w(\{n\}, i, a)$  are function of the energy difference, seen by the jumping particle between  $i$  and  $j$  sites. For an activated process, the jump probability is taken as :

$$w(\{n\}, i, a) = \omega_o \exp\left(-\frac{\mathcal{E}}{k_B T} n_{i+a'}\right) \\ = w_{i \rightarrow j}(\{n\})$$

where  $\omega_o$  is a constant prefactor,  $\mathcal{E}/k_B T$  is the reduced energy that we call  $\gamma$ ,  $k_B$  is the Boltzmann constant and  $u_i$  is the vector connecting the initial and final sites.

### B-The break down of the lattice occupation symmetry: Mean field treatment

Investigation of the time evolution of the concentration is done in the limit of the mean field approach; the time evolution of  $p(i)$  is given by the following equation,

$$\frac{\partial p(i)}{\partial t} = - \sum_{j-i} \langle J_{i,j}(\{n\}) \rangle \quad (6)$$

For systems with repulsive nearest neighbour interaction, the use of the lattice gas model allows the reproduction of the order-disorder transition characterized by the break down of the occupation symmetry of the lattice. Hence, we decide to distinguish between various sublattices. Then, square (triangular) lattice is supposed to be divided into two (three) interpenetrating sublattices A, B (A, B and C), in the way that any site of them say A would have two (three) nearest neighbours in each of the other sublattice B ( B and C) [9,10].

The average concentration evolution in time of each sublattice satisfies the equation (5).

Then, we obtain two (three) kinetic coupled equations:

$$\frac{\partial p^\alpha(i)}{\partial t} = - \sum_{a=j-i} \langle J_{i,j}^{\alpha\lambda}(\{n\}) \rangle \quad (7)$$

$$\langle J_{i,j}^{\alpha\lambda}(\{n\}) \rangle = w_{i \rightarrow j}^{\alpha\lambda} p^\alpha(i) (1 - p^\lambda(j)) - w_{j \rightarrow i}^{\lambda\alpha} p^\lambda(j) (1 - p^\alpha(i))$$

with the upper indexes  $\alpha=A, B$  or (A, B, C) and  $\lambda \neq \alpha$  are introduced to identify the sublattices.

The numerical resolution of those equations (7) leads to the results shown in figures(1,2) for the square lattice and figures (3,4) for the triangular lattice.

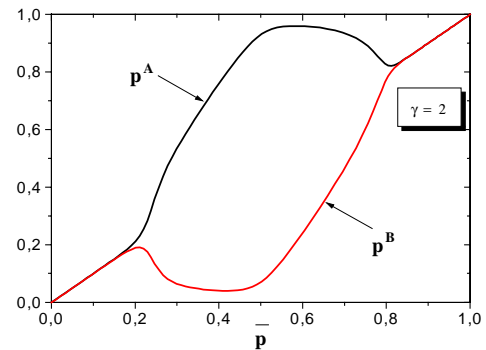


Fig.1: Occupation of the square sublattices A and B.

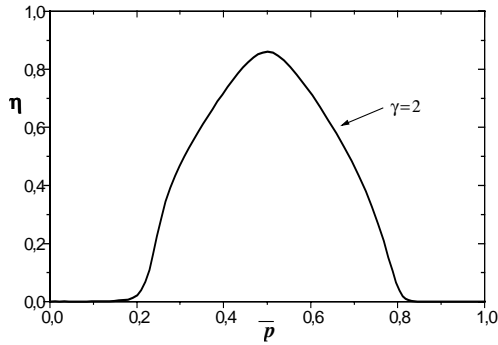


Fig.2 :Evolution of the order parameter  $\eta = p^A - p^B$  as a function of the mean concentration

We notice that the square lattice gas model with repulsive interaction presents an ordered phase Fig.1 and Fig.2, indeed we observe that one sublattice 'A' is occupied where the second 'B' is empty.

Fig. 3 shows, for different reduced energies, the variation of the concentrations of the three sublattices with respect to the average concentration of the system.

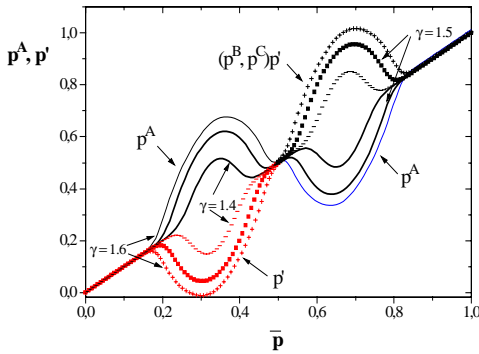


Fig. 3: The break down of the occupation symmetry of the triangular lattice

We notice that the lattice is disordered up to a minimum concentration which corresponds to the break down of occupation symmetry of the lattice. Then, we assist to the filling of one sublattice, the long range order corresponds to the commensurate phase of concentration  $\bar{p} = 1/3$ . The increase of average concentration leads the system to its disordered phase. The symmetry around  $\bar{p} = 0.5$  is a natural consequence of lattice gas model with interaction limited between pair of particles. One realizes the equivalence of the occupation of two sublattices. Then, the dynamic of the triangular lattice can be characterized by only one order parameter:

$$\eta = |p^A - p'|$$

where  $p' = (p^B + p^C)/2$  is the mean concentration of the identical sublattices.

The representation of  $\eta$  as a function of average concentration  $\bar{p}$  is shown in Fig. 4. We remark that the order parameter  $\eta$  presents maximums at the concentrations 1/3 et 2/3 relative to the formation of the ordered phases.

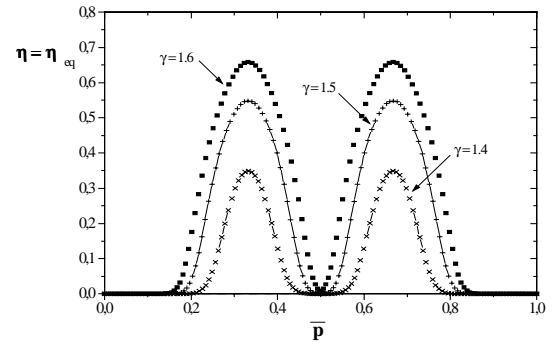


Fig.4: Evolution of the order parameter for different reduced energies. Arrows indicate different values of the reduced energies.

### III- MONTE-CARLO SIMULATIONS

The study of the dynamic of atoms on random media has led to the development of various sophisticated numerical methods as, Monte-Carlo procedures [11]. As an example, we treat in the framework of Kinetic lattice gas model the random jump to neighbouring empty sites of the chosen lattice. Particular attention is paid to the influence of order-disorder transitions in the diffusion of the ordered region. As an explicit example, the square and triangular lattice with repulsion between nearest neighbours.

#### A- Algorithm

The simulations have been performed on a semi - infinite lattice with periodic boundary conditions along the lateral side. For a given situation we start from a source where we choose randomly a particle; then if this particle jumps randomly to one of the first neighbour vacant sites, its site energy and that of the first neighbours particles of its initial position will change. So for every possible jump to the first neighbour sites we calculate the energy changes. The jump then occurs in one of the vacant sites with a probability proportional to the Boltzman factor with the appropriate energy difference and temperature.

The choice of the particle that jumps and the jump direction are identified by a random number  $0 \leq R \leq 1$ .

The dynamic of the system is controlled by the transition frequency  $w$  which encloses all the physical information of the considered system [11] and satisfies the detailed balance condition.

This transition frequency is proportional to  $\exp\left(-\frac{\Delta H}{k_B T}\right)$ , where  $\Delta H$  is either equal 0 or  $\varepsilon(N - N')$  and it represents the energy difference between initial and final state.

$$w_{i \rightarrow j} = w_o e^{-\varepsilon N / k_B T} \quad (8)$$

Where  $\varepsilon$  is the interaction energy ( $\varepsilon < 0$  with repulsive interaction).  $w_o$  is the Arrhenius factor chosen as the time of the simulation, following the Metropolis algorithm we write:

$$w_o = \min(1, e^{-(\Delta H / k_B T)}) \quad (9)$$

$N(N')$  is the number of the nearest neighbour particles of the initial (and final) site.

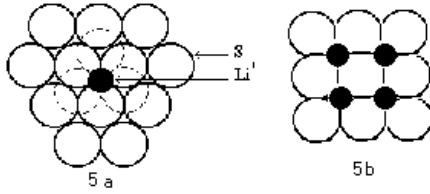


Fig 5.a Schematic illustration of the intercalated atoms (full circle) in a triangular grid of the interlayer octahedral holes.

Fig 5.b Represents a schematic view of the surface of the substrate, whose periodic potential provides a square lattice of preferred adsorption sites.

In this case the research has focused on the case of diffusing particles with repulsive nearest neighbour interaction [12,13], the other interactions are ignored. The key to the exact enumeration procedure is that the probability of a random walker being at any site ( $i$ ) at some time  $t$  (one can speak of time,  $t$ , or the  $t$ -th step as convenient) is determined by the probabilities of being at the nearest neighbours of the site ( $i$ ) at time ( $t-1$ ).

The simulation is a lattice gas simulation. The particles jump randomly on a square (triangular) lattice to the four (six) first neighbouring sites under the condition that if a given site is already occupied no other particle can jump it.

Experimentally diffusion (intercalation) is characterised by a concentration profile  $p(r,t)$ , where  $r$  is the position vector  $r(i, j)$ .

The average concentration is a function of time and space. As it follows we will consider only the situations obtained at fixed successive times. Both square and triangular lattices will be investigated.

If  $p(r,t)$  is bigger than the random number  $R$ , we put a particle in that site. In this way we constitute one detailed diffusion picture on which we look for the diffusion front [14-18] defined geometrically as the limit of the particles (solid circles) Fig.6 which are connected via first neighbours to the source.

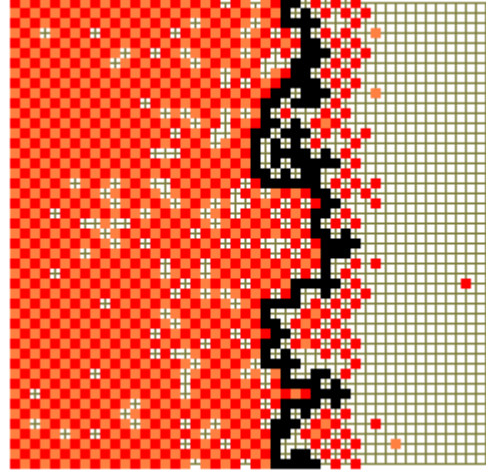


Fig.6: The diffusion front as a geometric place of the last infinite cluster connected to the source.

The dynamic of that object is developed in [15]. Indeed, very generally, the difficulty with the interacting case comes from the long range correlation and the appearance of phase transitions. In the simple case considered here two correlation lengths are present : a thermal one associated with a temperature  $T_c$  where a phase transition appears, and a percolation one associated with a concentration  $p_c$  where the infinite connected cluster appears.

### B-Square lattice

If one wishes to deal with a square lattice with the nearest neighbour interaction, one observes an ordered structure at  $\bar{p} = 0.5$ , and it is convenient to divide the lattice into 2 sublattices as indicated in Fig.7, and thus also introduces the sublattices densities  $p^A$  and  $p^B$ .

In terms of the  $p^A$  and  $p^B$  we express the long-range order parameter  $\eta = (p^A - p^B)/2$ .

The curve exhibits an ordered region around  $\bar{p} = 0.5$  where one of the two sublattices is occupied.

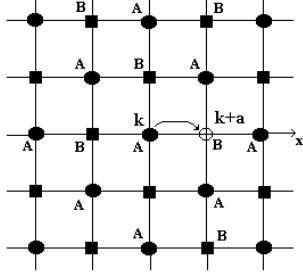


Fig.7 : Subdivision of the square lattice into two sublattices A and B.

Indeed, in Fig. 8 we confront the results of the mean field approach (continued line) and the Monte-Carlo calculation (dotted line), we remark that the methods are in good agreement.

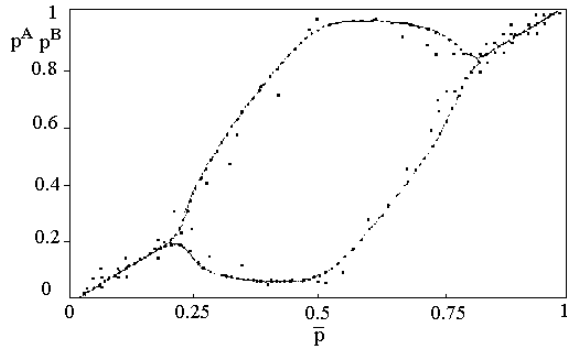


Fig.8: Representation of the sublattices concentrations  $p^A$  and  $p^B$  as a function of average concentration  $(p^A + p^B)/2$ , (... Monte Carlo results, — mean field result)

### C-Triangular lattice

subdivision of the triangular lattice into A, B and C sublattices, such as that any site in one of them say A has three nearest neighbours in each of the other two sublattices B and C.

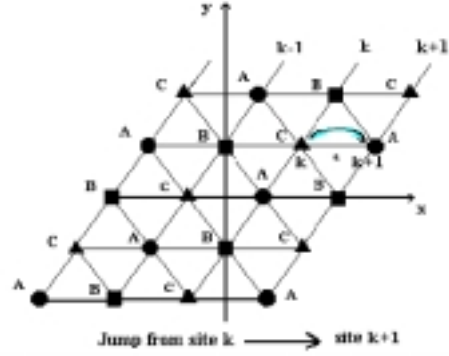


Fig.9: Schematic view of the triangular lattice subdivision

Analysis of the low temperature distribution of particles reported in the following figures gives clear evidence for some ordering of the particles on the 2D triangular intercalation lattice due to the particle-particle interaction.

General schemes of Monte-Carlo simulation of surface diffusion are shown below. In fact, we observe that a long range order can develop. Fig.10 shows the intercalated particle distributions for different concentrations ( $\bar{p} = 1/3, 1/2, 2/3$ ). In figure 11, we report the mean concentration  $\bar{p} = (p^A + p^B + p^C)/3$  as a function of position parameter  $x/L$ .

In figure 12, we remark that for  $\bar{p} = 1/3$  the tendency for local ordering along an  $\sqrt{3} \times \sqrt{3}$  superlattice appears clearly. For  $\bar{p} = 1/2$  one can see the tendency for forming alternatively full and empty parallel rows of sites. For  $\bar{p} = 2/3$  one observes the construction of the hexagonal superlattice complementary to the triangular  $\sqrt{3} \times \sqrt{3}$  one, obtained for  $\bar{p} = 1/3$ , where we can easily calculate that at this concentration the particles were randomly distributed on the octahedral sites plane with a long range order, so each particle would have only one particle in the first-neighbour.





Fig.10a: Schematic view of the simulation, the front is indicated by the bold points

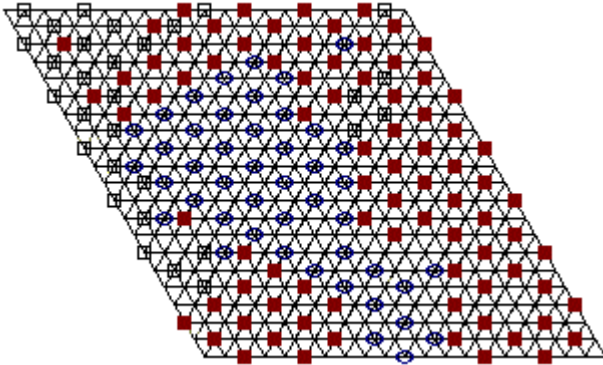


Fig.10b: Representation of the ordered region at  $\bar{p} = 1/3$ . (one sublattice occupied, two empty)

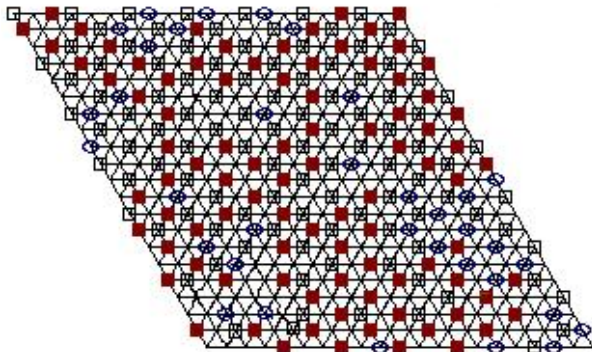


Fig.10c: Schematic view of the situation at  $\bar{p} = 0.5$ , we remark that system is disordered.

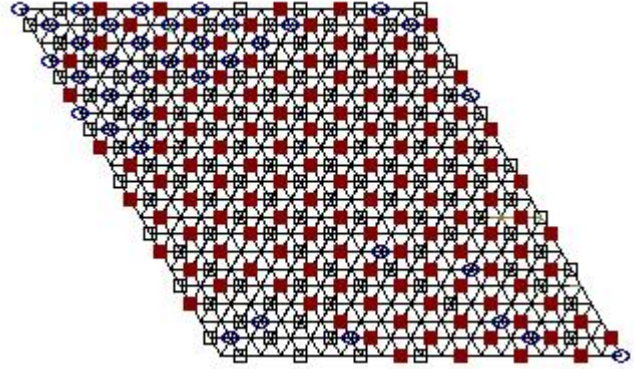


Fig.10d: At  $\bar{p} = 2/3$  we remark that the system present an ordered phase (two of the tree sublattices are occupied and one is empty)

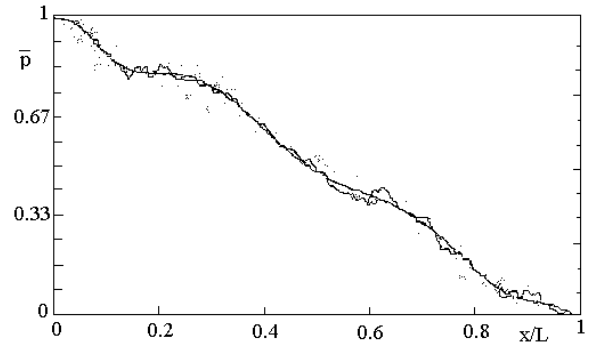


Fig.11: The concentration profile dependency on the coverage concentration  $\bar{p} = f(x/L)$ .

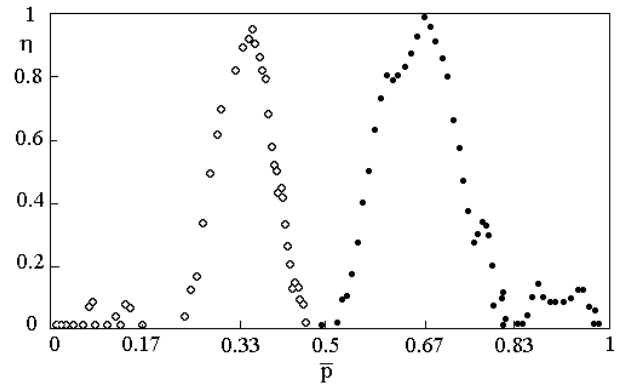


Fig.12: Evolution of the order parameter as a function of the coverage  $\bar{p} = (p^A + p^B + p^C)/3$

We remark that the lattice is disordered until a minimum concentration then, there appears ordered clusters, the growth of the ordered phase

corresponds to the filling of one sublattice A, at the concentration 0.33. The increase of the average concentration leads to the break down of the lattice order, at the half-full lattice ( $\bar{p} = 0.5$ ). Whereas, the order at  $\bar{p} = 2/3$  corresponds to the filling of two sublattices A and B. The result is in agreement with the mean field approach [13,20].

#### IV-CONCLUSION

With this work, the Monte-Carlo method is confirmed to be a very powerful tool for studying intercalation in adsorbed and lamellar compounds. The exact enumeration procedure may easily be continued up to time and memory limitations of the computer. The computation time increases linearly with the number of sites in the medium times the number of steps to which diffusion is performed. A comparison between the Monte-Carlo and the mean field results is also presented. A qualitative agreement is found between both results. The generalisation to other choices of interactions is the object of our perspectives.

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