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Statistical Models for Ensemble Control by Alloying and Poisoning of Catalysts

I. Mathematical Assumptions and Derivations

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The concentrations of ensembles of n surface atoms are usually assumed to be proportional to $(1 - \Theta)^n$ or $(1 - n\Theta)$, where Θ is the coverage of surface species passivating the surface atoms. In the present work a poison lattice model, taking into account the form of the ensembles, the ordering of the passivating atoms, and their radius of influence, is suggested. The general expression for ensemble concentrations is of the form $\Sigma_i q_i(1 - m\Theta)^{k_i}$, where q_i is a weight factor, m is the reciprocal coverage by the passivating atoms when they saturate the surface, and the k_i's are certain numbers (in general different from the number of atoms in the ensemble). In Part II (*J. Catal.*, **104**, 466 (1987)) the expressions are compared with Monte Carlo simulations and with experimental results. Also a short-range interaction model, giving analytical expressions for the concentrations of active sites and active pairs of sites, derived for the case where the passivating atoms are deposited randomly, but not on neighbor sites, on the (100) surface of a cubic crystal, i.e., corresponding to the local order in the $c(2 \times 2)$ structure, is discussed. © 1987 Academic Press, Inc.

1. INTRODUCTION

The effects of alloying and poisoning of metal catalysts are classical subjects of discussion. Usually in such discussions distinction has been made between the influence of geometric and electronic effects on the rate of catalytic reactions. Thus in some of the early works, 30–50 years ago, Balandin in his multiplet theory (*1*) and Kobozev in his ensemble theory (*2*) stressed the importance of geometric factors. With the advent of the band theory of the electronic states of solids, catalytic activity of transition metals and alloys containing transition metals were often related to the filling of the *d*-band (*3*).

In recent years, progress in experimental techniques and in theory has led to a modified picture in which the geometric and electronic effects have acquired a new meaning. First, it was found that the simple band theory did not work for many alloys. The atoms keep much of their individuality when they enter into an alloy. A surface of a random alloy AB, such as, e.g., Ni–Cu, can for the purpose of qualitatively describing chemisorption and reactions on it be pictured as a random mixture of atoms A and B each with electronic (and thus also chemical) properties resembling those of pure A and pure B, respectively (*4*).

From recent self-consistent quantum mechanical calculations has emerged a "local" description of the effect of foreign surface atoms which act as poisons or promoters. Nørskov *et al.* (*5*) have shown that electropositive atoms, like K, or electronegative atoms, like P, S, Cl, and O, adsorbed on metal surfaces will locally lower or increase, respectively, the electrostatic potential at the surface and thereby locally promote or poison, respectively, the chemisorption and dissociation of electron acceptor molecules, like H_2, O_2, N_2, and CO. Calculations indicate that the promoting or

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poisoning effect falls off within a few atomic distances from the foreign atom on the surface.

On the surface of a random alloy AB, "ensembles" of A atoms, consisting of a number of neighboring A atoms, will be present. Also on a metal surface with a random distribution of poisoning atoms ensembles of nonpoisoned neighboring metal atoms will be present. It has been found that the rate measured per active surface metal atom for some processes catalyzed by a transition metal A is affected very little by alloying A with an inactive metal B, while the rate per A atom in the surface decreases drastically for other processes when the B atoms are present in the surface (*6, 7*). The former processes are said to belong to group I and the latter to group II. The strong B atom dependence of the rate of group II processes is usually explained by assuming that the presence of ensembles of A atoms is necessary for the process. The much smaller dependences on alloying observed for group I processes are usually said to be the result of a "ligand" effect.

Also the strong influence of poisons on many catalytic processes has often been explained by assuming that the presence of ensembles comprising a minimum number of unpoisoned atoms is necessary for the process to take place.

Attempts to determine the critical size of the active ensembles have usually been based on expressions of the form

$$r = r_0(1 - a\Theta) \tag{1}$$

or of the form

$$r = r_0(1 - \Theta)^n \tag{2}$$

or combinations of (1) and (2). r_0 is the rate when no passivating or inactive atoms are present in the surface, and Θ is the coverage of the surface by passivating or inactive atoms. Two different coverage parameters are used in the following. (i) Θ is the expected (average) number of inactive or passivating surface atoms divided by the number, N_M, of atoms in a complete surface layer of active metal atoms without inactive or passivating atoms. (ii) Θ_p is the expected (average) number of inactive or passivating atoms divided by the number of atoms in an ideal saturation layer equal to the number, N_P, of possible sites for the inactive or passivating atoms. In many applications N_P is smaller than N_M, i.e., $N_P = N_M/m$, where m is an integer larger than 1 and consequently $\Theta_p = m\Theta$.

Maxted (*8*) used an expression of the form (1) to correlate the activity of deactivated catalysts with the concentration of poison on the catalyst. A simple Langmuir analysis leads to expression (2) in which n then is the number of metal atoms in the active ensemble. Expression (1) can be regarded as an approximation to (2) valid only at small coverages, i.e., $a = n$, or it can be used to describe in an approximate way a ligand effect, i.e., that more than one site is made inactive by a poison or inactive alloy atom or that the electronic properties of the neighboring metal atoms are changed.

Martin (*9*) used a combinatorial expression to determine the concentration of nonpoisoned ensembles. A (100) metal surface was considered and it was assumed that the poisoning atoms could chemisorb on the fourfold hollow sites of the surface. In the limit of a large surface, the classical expression (2) was obtained for nonpoisoned single atoms, pairs, and $m \times m$ ensembles with the exponent $n = (m + 2l - 1)^2$, where l is the neighbor number of the most distant metal atom influenced by the poisoning atom.

Martin *et al.* (*10*) used the same combinatorial expression to derive a particle size dependence for the concentration of nonpoisoned ensembles. This theory is briefly discussed in Part II (*11*).

Later, Martin (*12*) used a similar combinatorial expression to determine the probability that a square ensemble is active when a distribution of a constant number of equal square islands of poisoning atoms is present on the surface and from this Martin derived an expression for the concentration of nonpoisoned ensembles on a surface poisoned in this special way. This theory is also discussed in Part II.

Many LEED studies of clean transition metal surfaces with foreign atom overlayers show that long-range ordered surface structures with lattice unit cells larger than that of the clean surface are usually formed (*13*). Thus if sulfur atoms are chemisorbed at low pressure at room temperature on the Ni(100) surface a $p(2 \times 2)$ structure, corresponding to a Ni : S surface atom ratio of 4 : 1 at saturation, is formed at low coverages. At higher coverages the diffraction pattern changes into the one corresponding to the $c(2 \times 2)$ structure with a Ni : S surface atom ratio of 2 : 1 at saturation (*14*, *15*).

These observations imply that two sulfur atoms cannot chemisorb on neighboring sites and also that the final sticking of the sulfur atoms on allowed sites cannot be completely random as the diffraction pattern indicates order of macroscopic range.

The possible influence on the ensemble concentration due to mutual interaction of the passivating atoms, or a passivation range, or of the shape of the active ensembles has not been taken into account in previous theories.

In the present paper two new models of ensemble concentrations on the surfaces modified by inactive or poisoning atoms are presented. In the following paper (Part II) (*11*) the concentration of "active" ensembles of a specified form and size is calculated for some important cases and comparisons are made with stochastic numerical simulations and available experimental data.

In the first model, the *poison lattice model* (PLM) described in Section 2, the repulsive interaction between the poisoning atoms and the ordering tendency are approximately taken into account by restricting the positions of the poisoning atoms to the sites of a lattice corresponding to the positions of the poisoning atoms in the expected surface structure. The crystallography of the surface and the form and size of the ensembles have to be specified. It is further assumed that the passivating atoms have a radius of influence, i.e., one atom can passivate not only the site on which it is located, but also the nearest neighbor atoms or sites, and possibly also the next nearest neighbors or sites, etc.

If a finite metal surface lattice is considered, effects due to the finite size can be taken quantitatively into account as illustrated in the example in Section 2.

In the second model, the *short-range interaction model* (SRIM) described in Section 3, approximate, but highly accurate, expressions are derived for the concentrations of active sites and pairs as functions of the coverage of the surface by the poisoning atoms. In this model it is assumed that the poisoning atom passivates not only its own site but also the nearest neighbor sites. The poisoning atoms are assumed to occupy the sites of the surface at random while respecting the mutual repulsion between the poisoning atoms; i.e., a poisoning atom cannot have another poisoning atom on a neighbor site. The principal difference between the PLM and the SRIM is that in the latter model any site without poison atom neighbors can be occupied by a poison atom.

2. POISON LATTICE MODEL FOR ENSEMBLE CONTROL

In this section the poison lattice model is described without going into mathematical details. In Appendix A the mathematics of the model are presented in a rigorous way.

A finite flat surface formed by metal atoms is considered. An n-ensemble on the surface is defined as n neighboring surface metal atoms or n neighboring hollow sites between the metal atoms. An ensemble is characterized by its number of atoms (sites) as well as by the relative positions of the atoms (sites), i.e., its *shape*, e.g., row, equitriangular, rectangular, hexagonal.

Consider, as an example, an $M \times M$ quadratic lattice of hollow sites between metal atoms. Let Ω be the set of all possible rectangular 3 × 2 ensembles of sites. Ω will then comprise $2 \times (M-2) \times (M-1)$ distinct ensembles.

It is assumed that the poisoning atoms can occupy the sites of a sublattice of the lattice of hollow sites. This sublattice may be identical to the lattice of hollow sites but it may also have a unit cell larger than that of the metal atom lattice. The poison lattice can thus be chosen in such a way that the metal surface plus the fully occupied poison lattice corresponds to the chemisorption structure inferred from LEED measurements. For example, if sulfur poisoning of a (100) surface is considered at conditions where the $c(2 \times 2)$ array is known to be formed, only every second hollow site is assumed to belong to the poison lattice.

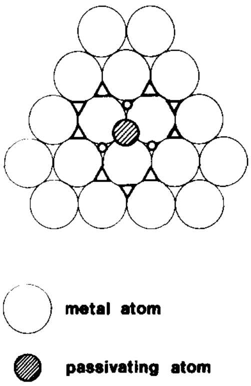
The probability Θ_p of adsorption of a poisoning atom on a site of the poison lattice is assumed to be independent of the position of the site and of the occupation of the other sites.

It is assumed that the poisoning atom can passivate neighboring atoms (sites) within a certain distance R, called the *passivation range*. If one or more of the atoms (sites) of an ensemble are passivated, then the ensemble is assumed to be passivated; otherwise it is considered to be active. Figure 1 shows, as an example, the passivation patterns of the threefold sites between the atoms of a hexagonal surface lattice of metal atoms for various values of R.

The probability p_Ω that an ensemble ω selected at random from the set Ω is active is, as shown in Appendix A, given by

$$p_\Omega = \sum_{k=0}^{\infty} q_k(1-\Theta_p)^k. \qquad (3)$$

The exponent k, called the *exposure number* of the ensemble, is equal to the number of poison lattice sites within the passivation range distance of at least one atom (site) of the ensemble. The weight factor q_k is the probability that the ensemble ω, selected at random, has the exposure number k. The sum of the expression (3) contains only a few terms with q_k different from zero.



Passivated sites	R
▨	0
▨+○	$\frac{1}{\sqrt{3}}$
▨+○+△	1
▨+○+△+▽	$\frac{2}{\sqrt{3}}$

FIG. 1. Sites passivated by an atom on a hexagonal surface for various passivation radii R.

The following simple example illustrates the determination of the k's and the q_k's: A quadratic surface with $M \times M = 10 \times 10$ metal atoms (shown as open circles in Fig. 2) is considered. It is assumed that the poisoning conditions correspond to the formation of a $c(2 \times 2)$ structure. Accordingly the lattice of the sites for the poisoning atoms is the lattice of crosses in Fig. 2. It is assumed that $R = \sqrt{2}/2 \times$ the unit length of the metal surface lattice. This passivation range corresponds to the passivation of nearest neighbor metal atoms (in contact with the poisoning atom) only.

Far from the edges of the metal lattice 2 × 2 ensembles of metal atoms can be arranged in two ways with respect to the poison lattice and with $k = 4$ and 5, respectively, as shown by ensembles 1 and 2 in Fig. 2. The total number of 2 × 2 ensembles on the surface is $(10-1) \times (10-1) = 81$. The ensembles along the edges have exposure numbers different from those far from the edges. The four corner ensembles have $k = 2$, while the 28 edge ensembles have $k = 3$. Of the remaining 49 ensembles, 25 have $k = 5$ and 24 have $k = 4$. Thus the final expression for the concentration of active

2×2 ensembles is

$$p_{2\times 2}(M = 10) = 25/81(1 - 2\Theta)^5 + 24/81(1 - 2\Theta)^4 + 28/81(1 - 2\Theta)^3 + 4/81(1 - 2\Theta)^2. \quad (4)$$

If we increase the number of metal surface atoms to infinity then the edge and corner contributions disappear and the infinite lattice expression becomes

$$p_{2\times 2}(M \rightarrow \infty) = \tfrac{1}{2}[(1 - 2\Theta)^5 + (1 - 2\Theta)^4] = (1 - \Theta)(1 - 2\Theta)^4. \quad (5)$$

Values of k and q_k for a number of other important cases with square or hexagonal surface atom or site lattices can be determined from the tables in Part II (*11*).

3. STATISTICAL SHORT-RANGE INTERACTION MODEL FOR ENSEMBLE CONTROL

The model described in Section 2 has the important property of conforming when the poison lattice is saturated with the long-range order, which is the basis of the LEED observations. It is obvious, however, that at low poison coverages this model will not correspond to a physically probable poison distribution when the unit cell of the poison lattice is larger than that of the metal surface lattice.

Models in which the sites for deposition of the poison atoms are selected at random, but with the restriction that the deposition cannot take place if the site is passivated by a previous deposition on or near the site, may in many cases be more realistic at low poison coverages. A particular example of such a short-range interaction model is considered below. A more extensive treatment of this type of model with derivations of expressions for several types of ensembles on square as well as hexagonal lattices will be published elsewhere (*16*).

As an example, the important case where, on a square lattice, poison deposition on nearest neighbor sites of the sites with a poison atom is prohibited, is treated below. Approximate, but very accurate, formulas for the concentrations of active single sites (singletons) and pairs of active sites (doublets) are derived. The self-poisoning of the poison deposition with a passivation range equal to the nearest neighbor distance corresponds to the short-range order in the $c(2 \times 2)$ structure of the (100) surface of cubic crystals.

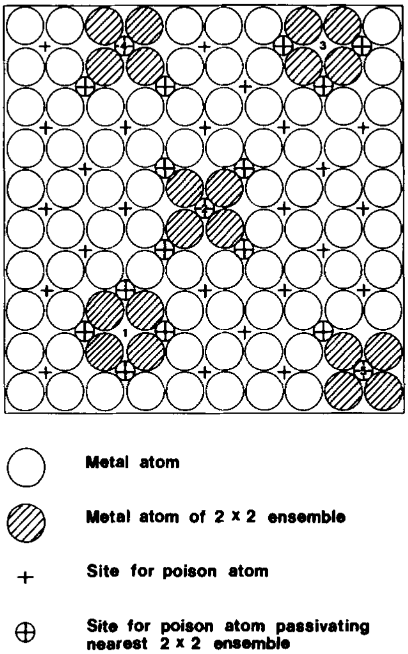


FIG. 2. 10 × 10 square metal atom lattice with five different 2 × 2 metal atom ensembles and a poison lattice consisting of every second fourfold hollow site (+). k values for $R = \sqrt{2}/2$: 1, internal ensemble with $k = 4$; 2, internal ensemble with $k = 5$; 3, edge ensemble with $k = 3$; 4, edge ensemble with $k = 3$; 5, corner ensemble with $k = 2$.

The probability that a site is active is called p_s, and the probability that a pair of neighboring sites are active is called p_d.

As the neighbor sites of an active ensemble must be unoccupied the following suggestive notation is used:

$$p_s = P_2\left(\begin{smallmatrix} & \text{o} & \\ \text{o} & \text{o} & \text{o} \\ & \text{o} & \end{smallmatrix}\right) \quad (6)$$

$$p_d = P_2\left(\begin{smallmatrix} & \text{oo} & \\ \text{o} & \text{oo} & \text{o} \\ & \text{oo} & \end{smallmatrix}\right). \quad (7)$$

A singleton corresponds to the presence of the configuration of unoccupied sites shown in Eq. (*6*), while a doublet corresponds to the configuration shown in Eq. (7). Here P means the probability of the configuration shown in parentheses, subscript 2 refers to the two-dimensional lattice, o means an unoccupied site, and x a site with an unspecified state of occupation.

Now,

$$p_s = P_2\left(\begin{array}{ccc} & o & \\ o & o & o \\ & o & \end{array}\right) = P_2\left(\begin{array}{ccc} & x & \\ o & o & o \\ & x & \end{array}\right) \cdot P_2\left(\begin{array}{ccc|ccc} & o & & & x & \\ x & o & x & o & o & o \\ & o & & & x & \end{array}\right).$$

$P_2\left(\begin{array}{ccc|ccc} & o & & & x & \\ x & o & x & o & o & o \\ & o & & & x & \end{array}\right)$ means the conditional probability that the three vertical sites of the singleton configuration (6) are unoccupied when the three horizontal sites are unoccupied.

The following approximations, both heuristically plausible, are made:

$$P_2\left(\begin{array}{ccc} & x & \\ o & o & o \\ & x & \end{array}\right) \sim P_1(ooo)$$

$$P_2\left(\begin{array}{ccc|ccc} & o & & & x & \\ x & o & x & o & o & o \\ & o & & & x & \end{array}\right) \sim P_2\left(\begin{array}{ccc|ccc} & o & & & x & \\ x & o & x & x & o & x \\ & o & & & x & \end{array}\right) \sim P_1(ooo|xox),$$

where subscript 1 refers to the one-dimensional model discussed in Appendix B. Thus,

$$p_s \sim P_1(ooo) \cdot P_1(ooo|xox).$$

By inserting the expressions B4 and B5 in Appendix B for the factors on the right-hand side the following expression is obtained:

$$p_s \simeq (1 - \Theta)\left(\frac{1 - 2\Theta}{1 - \Theta}\right)^4. \qquad (8)$$

An expression for p_d is obtained in a similar way:

$$\begin{aligned} p_d = {} & P_2\left(\begin{array}{cccc} & x & x & \\ o & o & o & o \\ & x & x & \end{array}\right) \cdot P_2\left(\begin{array}{cccc|cccc} & o & x & & & x & x & \\ x & o & x & x & o & o & o & o \\ & o & x & & & x & x & \end{array}\right) \\ & \cdot P_2\left(\begin{array}{cccc|cccc} & x & o & & & o & x & \\ x & x & o & x & o & o & o & o \\ & x & o & & & o & x & \end{array}\right) \sim P_1(oooo) \\ & \cdot P_2\left(\begin{array}{cccc|cccc} & o & x & & & x & x & \\ x & o & x & x & x & o & x & x \\ & o & x & & & x & x & \end{array}\right) \cdot P_2\left(\begin{array}{cccc|cccc} & x & o & & & o & x & \\ x & x & o & x & x & x & o & x \\ & x & o & & & o & x & \end{array}\right) \\ & \sim P_1(oooo) \cdot P_1(ooo|xox) \\ & \qquad \cdot P_1(xooox|oxoxo) \end{aligned}$$

which by means of B4, B5, and B7 finally gives

$$p_d \simeq (1 - \Theta)\left(\frac{1 - 2\Theta}{1 - \Theta}\right)^5 \frac{1}{\left(1 + \dfrac{(1 - \Theta)\Theta}{(1 - 2\Theta)^2}\right)^2} \qquad (9)$$

4. DISCUSSION

It has been known for a long time from LEED observations that many adsorbates modifying the catalytic properties of transition metal surfaces have a tendency to be chemisorbed into surface structures with unit cells larger than that of the clean surface. This fact, however, has not been taken into account in previous discussions of the influence of inactive or passivating surface atoms on the rate of catalytic reactions via an ensemble dependence.

The models of ensemble concentrations described in the previous sections take this tendency into account in an approximate way. The accuracy of the approximations is difficult to judge as very limited information is available regarding the process of the formation of the surface structure with the chemisorbed atoms and its dynamical behavior under reaction conditions. Several possibilities can be envisaged. The simplest corresponds to the SRIM described in Section 3, i.e., random occupation of sites with the constraint that an atom cannot be chemisorbed within the observed minimum distance from another chemisorbed atom.

The derivation of formulas for the concentration of active single sites and pairs of active sites was indicated for the case where a chemisorbed, passivating atom prevents the chemisorption of passivating atoms on nearest neighbor sites on a square lattice. Formulas for other cases will be published elsewhere. A drawback of this approach is that random chemisorption is not compatible with the fact that LEED patterns demonstrate the presence of surface structure with long-range order. On the other hand it is also observed that the LEED pattern corresponding to the surface structure of the chemisorbed atoms is, in many cases, replaced by the pattern corresponding to the clean surface when the surface is heated to high temperature (*17–19*). This may indicate that thermally generated disorder washed out the long-range order of the chemisorption structure, making it plausible that the SRIM might constitute a reasonable description of the distribution of the passivating atoms at the temperature of many reactions.

Introducing surface mobility of the adsorbing species before they are fixed on a surface site, i.e., assuming that chemisorption takes place through a mobile precursor, may enhance the growth of domains with sufficient long-range order for the formation of a LEED pattern. It is therefore of interest to investigate the effect of precursor mobility on the SRIM. This is done by means of Monte Carlo simulations in Part II (*11*).

The PLM developed in Section 2 has several advantages. It is generally applicable and formulas for any ensemble on any surface and passivation lattice and with any passivation range can easily be derived. The main assumption of this model, that the possible sites for passivating atoms form a fixed lattice with a unit cell equal to or larger than that of the clean surface, is in accordance with the LEED observations of long-range order at coverages near saturation. The fixed lattice assumption should not influence the accuracy of the formulas at small coverages unless long-range forces result in island growth even at small coverages. The correction at high coverages due to a few boundaries between domains not in registry is also expected to be small; e.g., in the case of the $c(2 \times 2)$ chemisorption structure on a (100) surface a boundary between two domains not in registry will give no correction to the expression for the concentrations of active sites and of pairs of active sites.

The PLM expression (3) for the concentration of ensembles can be considered as a generalization of the classical expression (2) to situations where ordering forces regulate the surface distribution of the passivating atoms and to situations where the passivating atoms, besides blocking their own sites, passivate nearby sites or metal atoms.

Hence, when experimental results are analyzed using expression (2), the exponent n need not correspond to the number of atoms in the critical ensemble, as is usually assumed. Moreover n need not be an integer. The observed exponent depends, in general, on the structure of the surface and the structure of the layer of passivating atoms, on the passivation range, on the shape of the critical ensemble, and on the surface coverage by passivating atoms.

In the simple PLM discussed at length in the present paper and in the succeeding paper (*11*), the passivating probability of the poison atoms is assumed to be zero outside and equal to 1 inside the passivation range. It is possible, as indicated by the expressions (A8) and (A9) in Appendix A, to generalize the PLM to take into account a gradual distance dependence of the passivation probability. A more general theory of this kind is obviously also more realistic, but it is at present too difficult to determine independently the extra parameters, $\rho(r)$, of expression (A9), to make such a generalization useful.

5. CONCLUSIONS

New theoretical models for the calculation of surface concentrations of ensembles of atoms or sites, active in chemisorption or reaction on partially passivated surfaces, are proposed. The models take into account the observation that chemisorbed atoms often form surface structures with unit cells larger than that of the clean metal surface. The ensemble concentration depends on the form and size of the ensembles. A passivation range has to be specified for the poison atoms. When the theory is applied to a finite surface lattice, ensembles near corners and edges will have a smaller probability of being passivated than ensembles far from edges.

Another type of model, called short-range interaction models and corresponding to a more random deposition of the poison atoms, is briefly discussed. Expressions for the concentrations of active sites and pairs on a (100) surface of a cubic crystal, on which the poison atoms cannot occupy neighbor sites, are given.

APPENDIX A

MATHEMATICAL TREATMENT OF THE STOCHASTIC POISON LATTICE MODEL

The models are based on two basic sets, the set Λ_M of M-sites and the set Λ_P of P-sites. The M-sites correspond to either the positions of the metal surface atoms or to the hollow sites between them. The P-sites correspond to possible surface locations for the poison atoms. In all concrete cases, Λ_M will be a set of lattice points in a regular planar lattice and Λ_P will either coincide with Λ_M or with the dual lattice of Λ_M, or Λ_P will only occupy a part of one of these lattices.

The number of M-sites and P-sites is denoted by N_M and N_P, respectively. It is assumed that the geometrical structure given by Λ_M and Λ_P, in particular the size numbers N_M and N_P, are fixed throughout the analysis.

An *ensemble* ω is defined as a subset of Λ_M. The number of M-sites in ω is denoted by $n(\omega)$. A *shape* Ω is a collection of ensembles all containing the same number of atoms or sites. For example, Ω could be the shape of 2×2 ensembles in a quadratic lattice. The common value of $n(\omega)$ for $\omega \in \Omega$ is called the *ensemble size* and is denoted by n. The number of *ensemble locations*, i.e., the number of ensembles in Ω, is denoted by N. Thus, if Ω is the shape of singletons (1×1 ensembles), the ensemble size is 1 and the number of ensemble locations N is equal to N_M. Each ensemble may be subject to passivation if nearby P-sites are occupied.

The basic assumptions are as follows:

(i) M-sites are occupied independently of each other and with the same probability Ψ.

(ii) P-sites are occupied independently of each other and with the same probability Θ_P.

(iii) An ensemble of shape Ω is selected at random with all N possibilities equally likely.

(iv) The random mechanisms of i–iii are independent of each other.

(v) Each occupied P-site passifies all M-sites within a given fixed passivation range R.

(vi) An ensemble ω is only active if all its M-sites are occupied and if none of these sites have been passified.

The independence assumptions in i, ii, and iv are essential for the calculations. If they fail, the results may well be affected in a significant way. Models with forbidden neighboring P-sites are handled by taking Λ_P as a lattice with a larger unit cell than Λ_M. In this way the essential independence can still be maintained (cf. Part II (*11*)).

Note that v and vi prescribe that each ensemble is either totally passified or not passified at all. Furthermore a circular pattern of passivation, viz., passivation of all M-sites within range R from an occupied P-site, has been chosen. In fact the present theory would work with any other passivation pattern.

Figure 1 shows as an example the passivation patterns of the threefold sites of a hexagonal surface lattice of metal atoms for various values of R.

Throughout the present and the accompanying paper (*11*) it is assumed that $\Psi = 1$; i.e., all the metal atom sites are occupied.

The number of occupied P-sites is denoted by Y. According to ii, this random variable has a binomial distribution with parameters N_P and Θ_P. Thus,

$$E(Y) = N_P \cdot \Theta_P, \quad \sigma^2(Y) = N_P \cdot \Theta_P \cdot (1 - \Theta_P) \quad \text{(A1)}$$

(E = expected value; σ^2 = variance). The coverage of Λ_P is then given by

$$E(Y/N_P) = \Theta_p, \quad \sigma^2(Y/N_P) = \Theta_p \cdot (1 - \Theta_p)/N_P. \quad (A2)$$

The coverage is thus almost a constant when N_P is large.

The probability that an ensemble chosen at random from Ω is active will be denoted p_Ω. The number of active ensembles of shape Ω is denoted X_Ω. Since X_Ω can be expressed as a sum over $\omega \in \Omega$ of the random variable assuming the value 1 if ω is active and assuming the value 0 otherwise, it follows that

$$E(X_\Omega) = N \cdot p_\Omega, \quad (A3)$$

which gives

$$p_\Omega = E\left(\frac{X_\Omega}{N}\right).$$

Therefore p_Ω corresponds to the concentration of active ensembles of shape Ω. In order to calculate p_Ω an *exposure number* is introduced for each $\omega \in \Theta$. By definition, this number is the number of P-sites j for which the occupation of j would passify ω.

The *exposure probabilities* q_k; k = 0, 1, 2, . . . , are defined by

q_k = probability that ω selected at random from Ω has exposure number k. (A4)

If N_k = number of $\omega \in \Omega$ with exposure number k, then according to iii,

$$q_k = N_k/N \quad k = 0, 1, 2, \ldots . \quad (A5)$$

The probability p_Ω is given by

$$p_\Omega = \sum_{k=0}^{\infty} q_k(1 - \Theta_p)^k. \quad (A6)$$

Note that there will only be a few values of k for which q_k is nonzero so that the apparent infinite sum in (A6) is, in fact, finite. Also note that assumption iii may be replaced by any other assumption on the random selection of ensembles of shape Ω. Formula (A6) is still valid, but (A5) can then no longer be used.

In the simple case when one of the exposure probabilities is close to 1, (A6) reduces to the single-term expression

$$p_\Omega = (1 - \Theta_p)^k, \quad (A7)$$

where k is the typical number of P-sites which can passify an ensemble.

If the passivation model is defined in such a way that the passivating atom has a distance-dependent passivation probability, $\rho(r)$, (A7) should be replaced by an expression of the form

$$p_\Omega = (1 - a_1\Theta_p)^{k_1}(1 - a_2\Theta_p)^{k_2} \cdots (1 - a_\nu\Theta_p)^{k_\nu}, \quad (A8)$$

where $k_1 + k_2 + \cdots + k_\nu = k$ and the a_i's are certain *ensemble passivation probabilities*. Each of the a_i's is given by an expression of the form

$$a_i = 1 - [1 - \rho(r_1)][1 - \rho(r_2)] \cdots [1 - \rho(r_n)], \quad (A9)$$

where $r_1, r_2, \ldots, r_n$ are the distances a fixed P-site could have to the n-sites in an ensemble of shape Ω if at least one of these distances is less than or equal to the passivation range R (in (A9) $\rho(r) = 0$ if $r > R$).

For instance, if $\Lambda_M = \Lambda_P$ is the quadratic lattice, Ω the shape of 2×2 ensembles and $r = \sqrt{2}$, then (A7) leads to

$$p_\Omega = (1 - \Theta_p)^{16} \quad (A10)$$

whereas (A9) gives

$$p_\Omega = (1 - a_1\Theta_p)^4(1 - a_2\Theta_p)^8(1 - a_3\Theta_p)^4 \quad (A11)$$

with

$$a_1 = 1 - (1 - \rho_0)(1 - \rho_1)^2(1 - \rho_2)$$
$$a_2 = 1 - (1 - \rho_1)(1 - \rho_3)$$
$$a_3 = 1 - (1 - \rho_2), \quad (A12)$$

ρ_0, ρ_1, and ρ_2 denoting the distance-dependent passivation probabilities. Note that (A11) reduces to (A10) if $\rho_0 = \rho_1 = \rho_2 = 1$.

Just as (A6) can be considered as a mixture of the expression (A7), the general formula for p_Ω in the model with distance-dependent passivation probabilities will be a mixture of the expressions (A9).

APPENDIX B

THE LINEAR SHORT-RANGE INTERACTION MODEL WITH NEAREST NEIGHBOR PASSIVATION

In the appendix the probabilities of various configurations on an infinite *linear* lattice are derived. The sites of the lattice are occupied at random by passivating atoms but with the constraint that there is at least one unoccupied site between two occupied ones. In fact, this description is too vague to define the model in a mathematically unambiguous way. A main interest of this appendix is to specify a well-defined model[1] and to carry out exact calculations in this model. Additionally, of course, the results are needed in the main text.

The number of different ways k-occupied sites can be distributed among the n-sites of a linear lattice (it being understood that occupied neighbors are forbidden) is denoted by $r_{n,k}$. Then

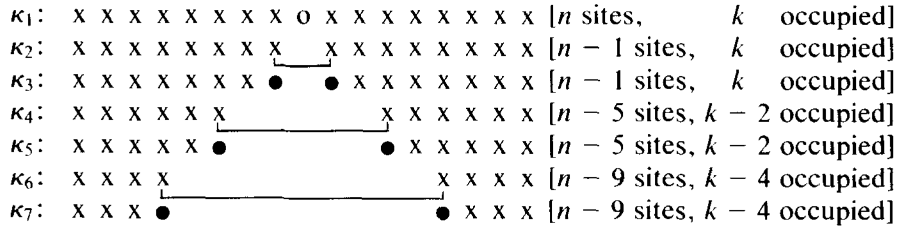
$$r_{n,k} = \binom{n-k+1}{k} \tag{B1}$$

(indeed, choose k sites among $n - k + 1$ linearly ordered sites, insert an unoccupied site to the right of every one of the k chosen sites, and lastly remove the site lying furthest to the right; in this way all the designed $r_{n,k}$ configurations may be obtained and the result follows).

The infinite linear lattice, for which the formulas are derived below, is obtained by letting the finite linear lattice grow in a symmetric way and such that $k \approx \Theta n$. The calculations performed in this model concern sites centrally situated in the lattice. The method of calculation is illustrated by calculating $P(\mathrm{o})$, the probability that a fixed site is unoccupied. Of course, $P(\mathrm{o})$ must be $1 - \Theta$, but this has to be proved using the model. Assume that n is very large, that $k \approx \Theta n$, and that the site in question is centrally situated in the lattice. Then $P(\mathrm{o})$ may be approximated by the corresponding probability in the finite n-size model; i.e.,

$$P(\mathrm{o}) \approx \frac{a_{n,k}}{r_{n,k}}, \tag{B2}$$

where $a_{n,k}$ is the number of those configurations among the $r_{n,k}$ configurations which leaves the site indicated unoccupied. Consider the following configurations (indicated for the case $n = 17$):



A bracket connecting two sites indicates that the sites should be considered neighbors. For the configurations κ_1–κ_7 it is still understood that occupied neighbors are forbidden. For κ_3, two of the k-occupied sites have been fixed. Similarly for κ_5 and κ_7. The number of ways in which the configuration κ_i can be obtained is denoted by $\#(\kappa_i)$.

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[1] The reader should be warned that the two-dimensional case which is the one that interests us, and which is discussed in Section 3, has in fact not been specified in a mathematically satisfactory way. Such a specification and associated precise calculations are a highly delicate matter (connected with the theory of random Markov fields, known from certain very recent studies both of mathematical and of theoretical statistical physics).

From the definition of the configurations κ_i it is seen that

$$a_{n,k} = \#(\kappa_1) = \#(\kappa_2) + \#(\kappa_3) = r_{n-1,k} + \#(\kappa_3),$$

$$\#(\kappa_3) = \#(\kappa_4) + \#(\kappa_5) = r_{n-5,k-2} + \#(\kappa_5),$$
$$\#(\kappa_5) = \#(\kappa_6) + \#(\kappa_7) = r_{n-9,k-4} + \#(\kappa_7),$$

and so on. Hence,

$$a_{n,k} = r_{n-1,k} + r_{n-5,k-2} + r_{n-9,k-4} + \cdots$$

so that (B2) becomes

$$P(\mathrm{o}) = \lim_{n\to\infty} \frac{1}{r_{n,k}} \sum_{i\geq 0} r_{n-1-4i,k-2i}. \qquad \text{(B3)}$$

The sum in (B3) is in fact finite since $n - 1 - 4i \geq 1$ must hold; i.e., $i \leq (n - 2)/4$ (in the extreme case $k = (n + 1)/2$, the sum is empty, and hence has the value 0).

Recalling that $k \approx \Theta n$ (k may be taken as the integer part of Θn), it only takes some trivial manipulations with binomial coefficients to deduce from (B1) and (B3) that, as claimed,

$$P(\mathrm{o}) = 1 - \Theta.$$

The following expression is obtained by the same method

$$P\left(\underbrace{\mathrm{oo}\cdots\mathrm{o}}_{\nu}\right) = \lim_{n\to\infty} \frac{1}{r_{n,k}} \sum_{i\geq 0} r_{n-\nu-4i,k-2i}$$
$$= \lim_{n\to\infty} \frac{1}{r_{n-\nu+1,k}} \sum_{i\geq 0} r_{n-\nu-4i,k-2i} \cdot \lim_{n\to\infty} \frac{r_{n-\nu+1,k}}{r_{n,k}}$$

which, by the previous result, gives

$$P\left(\underbrace{\mathrm{oo}\cdots\mathrm{o}}_{\nu}\right) = (1 - \Theta)\left(\frac{1 - 2\Theta}{1 - \Theta}\right)^{\nu-1}. \qquad \text{(B4)}$$

Note that for $\nu = 1$ this contains the above result $P(\mathrm{o}) = 1 - \Theta$.

Expressions for $P(\mathrm{ooo}|\mathrm{xox})$ and $P(\mathrm{xooox}|\mathrm{oxoxo})$ are needed in Section 3. The first calculation is easy since it follows directly from the definition of conditional probability that $P(\mathrm{ooo}|\mathrm{xox}) = P(\mathrm{ooo})/P(\mathrm{o})$. Then, by (B4), we have

$$P(\mathrm{ooo}|\mathrm{xox}) = \left(\frac{1 - 2\Theta}{1 - \Theta}\right)^2. \qquad \text{(B5)}$$

The following expression is used to calculate the other conditional probability

$$P(\mathrm{xooox}|\mathrm{oxoxo}) = P(\mathrm{ooooo})/[P(\mathrm{ooooo}) + P(\mathrm{o{\bullet}ooo}) + P(\mathrm{ooo{\bullet}o}) + P(\mathrm{o{\bullet}o{\bullet}o})] \qquad \text{(B6)}$$

which by the same method gives

$$P(\mathrm{xooox}|\mathrm{oxoxo}) = \lim_{n\to\infty} \frac{A}{A + 2B + C},$$

where

$$A = \sum_i r_{n-5-4i,k-2i}$$

$$B = \sum_i r_{n-5-4i,k-2i-1}$$

$$C = \sum_i r_{n-5-4i,k-2i-2}.$$

Writing

$$\frac{A}{A + 2B + C} = \frac{A/r_{n-4,k}}{A/r_{n-4,k} + 2B/r_{n-4,k-1} \cdot r_{n-4,k-1}/r_{n-4,k} + C/r_{n-4,k-2} \cdot r_{n-4,k-2}/r_{n-4,k}}$$

in the limit $n \to \infty$ this expression becomes

$$P(\mathrm{xooox}|\mathrm{oxoxo}) = \frac{1 - \Theta}{(1 - \Theta) + 2(1 - \Theta)\dfrac{(1 - \Theta)\Theta}{(1 - 2\Theta)^2} + (1 - \Theta)\dfrac{1 - \Theta)^2\Theta^2}{(1 - 2\Theta)^4}}$$

or

$$P(\mathrm{xooox}|\mathrm{oxoxo}) = \frac{1}{\left(1 + \dfrac{(1 - \Theta)\Theta}{(1 - \Theta)^2}\right)^2}. \qquad \text{(B7)}$$

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