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Statistical aspects of the diffuse LEED problem

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Abstract. Diffuse low-energy electron diffraction (LEED) intensities can be observed in all situations where the surface cannot be represented by a perfect biperiodic array of atoms or molecules. For instance, this occurs when binding sites are either occupied or not by atoms, when several atoms or molecules are co-adsorbed, when one adsorbed species can be located at several possible binding sites, etc. So far, the statistical aspects of this problem have been disregarded. In fact, under certain circumstances, it is possible to extract from diffuse intensities a quantity that only depends on the local atomic arrangement near a binding site. A method based upon this possibility has been systematically used in all diffuse LEED studies and consequently these studies have been totally devoted to the determination of this local atomic arrangement. We show in this paper that this method only works if *one* binding site is occupied or not (binary chemisorption). In the other cases, investigation of diffuse LEED intensities requires knowledge of the statistical distribution of occupied sites and thus the statistical aspects of this problem can no longer be bypassed. For this reason and also because this problem is intrinsically interesting, we particularly focus on it here. Diffuse LEED intensity can be approximated by a sesquilinear form of the form factors for each adsorbed species. The coefficients of this form are the Fourier transforms on the two-dimensional surface lattice of the site-occupancy pair correlation functions. A self-consistent molecular-field approximation of these correlation functions is given in this paper. Particularly, the validity of this approximation is discussed in detail for the binary chemisorption case. Diffuse LEED intensities are provided in some other cases: (i) two kinds of atom are distributed at the surface of a binary metallic alloy; (ii) two adsorbed species coexist at a single crystal surface. We arrive at the conclusion that investigation of diffuse LEED intensities generally requires the direct comparison of measured and calculated intensities. In this way, we have to consider the local arrangement of atoms near occupied binding sites together with their statistical distribution at the surface.

1. Introduction

1.1. Previous work

In a previous paper, referred to as I (Le Bossé *et al* 1988), we give a general expression of the incoherent intensity (or diffuse low-energy electron diffraction (LEED) intensity)

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of electrons back-scattered at a single crystal surface partially covered with a disordered overlayer. More precisely, the relative incoherent intensity per unit of solid angle, in the direction (θ_f, φ_f) of the electron detector, is given by (in I, the ratio $k_{f\perp}^2/|K_{f\perp}|^2$ has been omitted)

$$I_{\text{incoh}}(\mathbf{k}_f^- \leftarrow \mathbf{k}_i^+) = \frac{4\pi^4 k}{A k_{i\perp}} \sum_{p=1}^{p_{\text{max}}} \sum_{p'=1}^{p_{\text{max}}} \frac{k_{f\perp}^2}{|K_{f\perp}|^2} S(p, p', \mathbf{k}_{f\parallel} - \mathbf{k}_{i\parallel}) \times \bar{K}_1(p, \mathbf{k}_f^- \leftarrow \mathbf{k}_i^+) K_1(p', \mathbf{k}_f^- \leftarrow \mathbf{k}_i^+). \quad (1)$$

In this expression, $k = E^{1/2}$ (E is the energy of the primary electron beam), A is the unit-cell area, and \mathbf{k}_i^+ and \mathbf{k}_f^- are respectively the wavevectors of incident and back-scattered electrons outside the single crystal. Denoting as θ_i the angle of incidence, $k_{i\perp} = E^{1/2} \sin \theta_i$ is the component of \mathbf{k}_i^+ perpendicular to the surface and $k_{f\perp} = E^{1/2} \sin \theta_f$ is the same component for \mathbf{k}_f^- . On the other hand, if \mathbf{K}_f^- is the wavevector of back-scattered electrons inside the crystal,

$$K_{f\perp} = (E - V_{\text{opt}} - \|\mathbf{k}_{f\parallel}\|^2)^{1/2} \quad (2)$$

represents its component perpendicular to the surface. In expression (2), V_{opt} is the optical potential of the substrate. As seen in I, $K_1(p)$ is the effective transition matrix of the reference site 1 in the chemisorption state p and $S(p, p')$ is the structure factor of the overlayer. Using here the same convention as in I, the chemisorption state $p = 0$ always corresponds to a vacancy. In the case $p_{\text{max}} = 1$, which represents for instance the adsorption of an atom at a well defined site of the surface, I_{incoh} simply reduces to the product of a form factor by a structure factor (Saldin *et al* 1985). We shall see that, in other cases, I_{incoh} has a more complicated expression. The way of evaluating K_1 is described in detail in I. However, in most of the cases that are examined in this paper, we can make one of the following assumptions at least: (i) surface coverage in atoms or molecules is low; (ii) adsorbed atoms or molecules are weak scatterers. In this way, incoherent intensity can be evaluated by only taking into account processes involving at most one single scattering event inside the overlayer. The evaluation of $K_1(p)$ becomes simpler than in the general case treated in I and leads to the expression

$$K_1(p, \mathbf{k}_f^- \leftarrow \mathbf{k}_i^+) = t_1(p, \mathbf{k}_f^- \leftarrow \mathbf{k}_i^+) + \sum_{\{g\}} t_1(p, \mathbf{k}_f^- \leftarrow \mathbf{k}_{ig}^-) M_S(\mathbf{k}_{ig}^- \leftarrow \mathbf{k}_i^+) + \sum_{\{g\}} \frac{K_{f\perp}}{K_{ig\perp}} M_S(\mathbf{k}_f^- \leftarrow \mathbf{k}_{ig}^+) t_1(p, \mathbf{k}_{ig}^+ \leftarrow \mathbf{k}_i^+) + \sum_{\{g_1\}} \sum_{\{g_2\}} \frac{K_{f\perp}}{K_{ig_2\perp}} M_S(\mathbf{k}_f^- \leftarrow \mathbf{k}_{ig_2}^+) t_1(p, \mathbf{k}_{ig_2}^+ \leftarrow \mathbf{k}_{ig_1}^-) M_S(\mathbf{k}_{ig_1}^- \leftarrow \mathbf{k}_i^+) \quad (3a)$$

where $K_{ig\perp}$ is given by

$$K_{ig\perp} = (E - V_{\text{opt}} - \|\mathbf{k}_{f\parallel} + \mathbf{g}\|^2)^{1/2} \quad (3b)$$

and M_S is the scattering amplitude of the substrate†. In expression (3a) $t_1(p)$ is the transition matrix of reference site 1 in chemisorption state p . In the momentum representation we have

$$t_1(p, \mathbf{k}_1^{s_1} \leftarrow \mathbf{k}_2^{s_2}) = \frac{2}{\pi} \sum_{L_1, L_2} Y_{L_1}(\mathbf{k}_1^{s_1}) t_1(p, L_1, L_2) Y_{L_2}^*(\mathbf{k}_2^{s_2}) \quad (4)$$

where labels s_1 and s_2 are + or -. When adscatterers are adatoms, we can easily express

† Note that there is a slight difference compared with I. The evaluation of M_S involves a displacement of the substrate in such a way that the reference site of the overlayer is located at the origin of space.

$t_1(p)$ in terms of the adatom phase shifts $\delta_1^{(p)}$ for the incident energy E and the optical potential V_{opt} inside the overlayer:

$$t_1(p, L_1, L_2) = \frac{1 - \exp(2i\delta_{l_1}^{(p)})}{2i(E - V_{\text{opt}})^{1/2}} \delta_{l_1 l_2} \delta_{m_1 m_2}. \quad (5)$$

In I, the statistical aspects of the diffuse LEED problem have not been actually taken up. As a matter of fact, we have only considered the particular case of binary chemisorption where a given chemisorption site is occupied or not, and we have restricted ourselves to the following situations: (i) adsorbates are randomly distributed at 2D surface lattice sites; (ii) two adsorbates cannot coexist at two adjacent sites and occupancies of two non-adjacent sites are not correlated. However, we have shown in this work that a general treatment of the statistical aspects of the diffuse LEED problem requires the determination of the Fourier transform on the surface lattice of the site-occupancy pair correlation function:

$$S(p, p', \mathbf{k}_{\parallel} - \mathbf{k}'_{\parallel}) = \sum_{j=1}^N \Gamma_{j1}(p, p') \exp[-i(\mathbf{k}_{\parallel} - \mathbf{k}'_{\parallel})\mathbf{T}_j] \quad (6a)$$

$$\Gamma_{j1}(p, p') = \langle n_j(p)n_1(p') \rangle - \langle n_j(p) \rangle \langle n_1(p') \rangle. \quad (6b)$$

In expression (6a), the vector \mathbf{T}_j defines the location of the j th site of the 2D surface lattice, and in expression (6b), $n_i(p_i)$ is the occupancy operator of site i for chemisorption state p_i . This operator is defined by

$$n_i(p) = \sum_{p_1=0}^{p_{\max}} \dots \sum_{p_{i-1}=0}^{p_{\max}} \sum_{p_{i+1}=0}^{p_{\max}} \dots \sum_{p_N=0}^{p_{\max}} |p_1 \dots p_{i-1} p p_{i+1} \dots p_N\rangle \times \langle p_1 \dots p_{i-1} p p_{i+1} \dots p_N|. \quad (7)$$

As in I, $|p_1 \dots p_N\rangle$ denotes a state vector that characterises the particular overlayer configuration in which site 1 is in the chemisorption state p_1, \dots , site N is in the chemisorption state p_N . In expressions (6), averages are performed over a grand canonical ensemble for which the density matrix is of the form

$$\rho = \frac{\exp[-\beta(\mathcal{H} - \mu\mathcal{N})]}{\text{tr}\{\exp[-\beta(\mathcal{H} - \mu\mathcal{N})]\}}. \quad (8)$$

So, evaluation of averages requires knowledge of a Hamiltonian \mathcal{H} , which describes interactions between adatoms or admolecules and between adsorbate and substrate. We assume that interactions between adatoms or admolecules are described in terms of pair interactions and we define for each chemisorption state p an adsorption energy $E_{\text{ads}}(p)$. So, the pseudo-Hamiltonian denoted by $\mathcal{H} - \mu\mathcal{N}$ in (8) is of the form

$$\begin{aligned} \mathcal{H} - \mu\mathcal{N} = & - \sum_{i=1}^N \sum_{p=1}^{p_{\max}} [E_{\text{ads}}(p) + \mu_i(p)] n_i(p) \\ & + \frac{1}{2} \sum_{i,j=1}^N \sum_{p,p'=1}^{p_{\max}} U_{ij}(p, p') n_i(p) n_j(p'). \end{aligned} \quad (9)$$

We implicitly assume here that $U_{ii}(p, p') = 0$. At the end of the calculations, we shall consider that all the chemical potentials $\mu_i(p)$ are site-independent.

1.2. Physical information contained in incoherent intensity

Expression (1) shows that incoherent intensity is a sesquilinear form of the effective transition matrix $K_1(p)$ of reference site 1. The coefficients of this form are nothing

other than the Fourier transforms on the 2D surface lattice of site-occupancy pair correlation functions $\Gamma(p, p')$. So, two kinds of physical information are contained in this intensity: (i) information about the geometrical structure of adsorbate plus substrate complex; (ii) information about the statistical distribution of adsorbates at the 2D surface lattice sites. Let us first remember that a chemisorption state p denotes an adsorbate located at a well defined binding site of the surface. So, the effective transition matrix $K_1(p)$ contains information about the geometrical arrangement of atoms which comprise adsorbate p and about their position with respect to the substrate atoms. On the other hand, $K_1(p)$ does not depend on the statistical distribution of adsorbate p at the 2D surface lattice sites. Conversely, the Fourier transform $S(p, p')$ of the site-occupancy pair correlation function $\Gamma(p, p')$ depends on this statistical distribution but does not depend on the geometrical structure of adsorbate p and p' surrounded by their neighbouring substrate atoms.

In the particular case of binary chemisorption, the incoherent intensity reduces to the product of a form factor $|K_1(1)|^2$ by a structure factor $S(1, 1)$. In this case, using the fact that S only depends on $k_{\parallel} - k_{\parallel}$, both kinds of physical information mentioned above can be easily separated by studying the logarithmic derivative L of the incoherent intensity with respect to incident energy E at constant $k_{\parallel} - k_{\parallel}$ (Saldin *et al* 1985). The singularities appearing in this logarithmic derivative can be eliminated by introducing Pendry's Y function of L and of the absorption potential $\text{Im}(V_{\text{opt}})$ (Pendry 1980). Then, comparison of measured and calculated Y functions allows one to extract physical information about the geometrical structure of the adsorbate plus substrate complex without having to determine the structure factor. Let us now remark that if the particular dependence of $S(p, p')$ on the difference $k_{\parallel} - k_{\parallel}$ allows one to eliminate the structure factor, there is no particular dependence of $K_1(p)$ on k_{\parallel} and k_{\parallel} , which allows one to eliminate the form factor by using a similar process. So, the investigation of short-range order inside the overlayer can only be carried out by directly comparing measured and calculated intensities. Obviously, geometrical parameters that determine the form factor have to be determined preliminarily from Pendry's Y function method. Then, the good statistical distribution of adsorbates leads to the best fit between calculated and measured intensities.

Unfortunately, expression (1) for the incoherent intensity clearly shows that the previous separation into both kinds of physical information is no longer possible in the case $p_{\text{max}} > 1$. Then, the Y function method cannot be applied and consequently studies of diffuse LEED intensity have to be carried out by directly comparing measured and calculated incoherent intensities. Even if we are only interested in the geometrical structure of adsorbate plus substrate complex, the structure factor determination can no longer be avoided as in the binary chemisorption case.

1.3. Aim of this paper

In this paper, we give a simple statistical treatment of the diffuse LEED problem in the case of a surface partially covered with one or several kinds of adsorbate. This treatment, based upon a molecular-field approximation, allows one to treat the case of a sparsely populated top layer in which a strong repulsive coupling between adsorbates exists. This treatment also works in all cases where the interaction energy between adsorbates is below kT . Structure factor S and average occupancy of each chemisorption state can be evaluated self-consistently, in terms of temperature, adsorption energies, chemical and pair interaction potentials. Some particular cases will be examined to illustrate this

problem. The simplest one, which we call binary chemisorption, corresponds to the chemisorption of an atom or a molecule at well defined sites of the surface. In these cases, the number of chemisorption states is 2: $p = 0$ corresponds to a vacancy and $p = p_{\max} = 1$ corresponds to the presence of an adsorbate. In this case, we carefully examine the validity of our statistical treatment in the strong-coupling limit. We also investigate two particular cases corresponding to $p_{\max} = 2$. First, we consider a binary alloy with a surface segregation leading to an almost complete surface atomic layer. We also consider the case of a sparsely populated overlayer that contains two kinds of chemisorption states, which may describe the same adsorbate located at two different chemisorption sites or two different adsorbates located at well defined sites. In these two cases, expressions for incoherent intensities are given and experiments illustrating the second case are discussed.

2. Statistical treatment of diffuse LEED

2.1. Molecular-field approximation

Let us calculate the average of the operator $\mathcal{H} - \mu\mathcal{N}$. In a first stage, we consider that adsorbates are randomly distributed on the 2D surface lattice sites. Then, for distinct sites i and j we have

$$\langle n_i(p)n_j(p') \rangle = \langle n_i(p) \rangle \langle n_j(p') \rangle \quad (10a)$$

and consequently we obtain

$$\begin{aligned} \langle \mathcal{H} - \mu\mathcal{N} \rangle = & - \sum_{i,p} [E_{\text{ads}}(p) + \mu_i(p)] \langle n_i(p) \rangle \\ & + \frac{1}{2} \sum_{i,j} \sum_{p,p'} U_{ij}(p,p') \langle n_i(p) \rangle \langle n_j(p') \rangle. \end{aligned} \quad (10b)$$

In a second stage, we consider the case where the overlayer is partially ordered. In this way, equation (10a) is no longer valid and $\langle n_i(p)n_j(p') \rangle$ has to be evaluated by using the general expression (6b) of $\Gamma_{ij}(p,p')$. Then, we can easily show that $\langle \mathcal{H} - \mu\mathcal{N} \rangle$ has the same form as in expression (10b) except that the pair interaction potential U occurring in this expression is replaced by an effective pair interaction potential U^* defined by

$$U_{ij}^*(p,p') = U_{ij}(p,p') \left(1 + \frac{\Gamma_{ij}(p,p')}{\langle n_i(p) \rangle \langle n_j(p') \rangle} \right). \quad (11)$$

The physical meaning of this effective potential clearly appears by examining the relation

$$\sum_{j,p'} U_{ij}^*(p,p') \langle n_j(p') \rangle = \sum_{j,p'} U_{ij}(p,p') \langle n_j(p') \rangle_{ip} \quad (12a)$$

which can be established from (11). As defined in I, $\langle n_j(p') \rangle_{ip}$ is the average site occupancy of adsorbate p' at site j calculated over a subset of the grand canonical ensemble in which all configurations $|p_1, p_2, \dots, p_N\rangle$ have the following property: site i is in chemisorption state $p_i = p$. It follows that

$$\langle n_j(p') \rangle_{ip} = \frac{\langle n_i(p)n_j(p') \rangle}{\langle n_i(p) \rangle}. \quad (12b)$$

Both sides of (12a) are nothing other than the average potential at site i when this site is

occupied by adsorbate p . This interpretation is obvious if we examine the right-hand side of (12a) in which average site occupancy of adsorbate p' at any site $j \neq i$ is calculated by assuming that adsorbate p is located at site i . This means that occupancies for different sites are correlated. Let us note that (12a) could be considered as a definition of U^* . In fact, (12a) allows us to deal with the actual average site occupancies $\langle n_i(p) \rangle$, that is to say the surface coverages of each adsorbed species, which can be drawn from experiment. In return, correlation effects are taken into account by using an effective pair interaction potential U^* .

Let us now write $n_i(p)$ in the form of a sum of its average and the deviation from this average:

$$n_i(p) = \langle n_i(p) \rangle + \delta n_i(p). \quad (13)$$

Then, putting (13) back into expression (9) for $\mathcal{H} - \mu\mathcal{N}$ and using the fact that $U_{ij}(p, p') = U_{ji}(p', p)$, we get

$$\mathcal{H} - \mu\mathcal{N} = \mathcal{H}_0 - \mu\mathcal{N} + \delta\mathcal{H} \quad (14a)$$

$$\begin{aligned} \mathcal{H}_0 - \mu\mathcal{N} = & - \sum_{i,p} \left(E_{\text{ads}}(p) + \mu_i(p) - \sum_{j,p'} U_{ij}(p, p') \langle n_j(p') \rangle \right) n_i(p) \\ & - \frac{1}{2} \sum_{i,p} \sum_{j,p'} U_{ij}(p, p') \langle n_i(p) \rangle \langle n_j(p') \rangle \end{aligned} \quad (14b)$$

$$\delta\mathcal{H} = \frac{1}{2} \sum_{i,p} \sum_{j,p'} U_{ij}(p, p') \delta n_i(p) \delta n_j(p'). \quad (14c)$$

As $\mathcal{H}_0 - \mu\mathcal{N}$ and $\delta\mathcal{H}$ are operators that commute, we can easily show that the average of any physical quantity \mathcal{A} depending on operators $n_i(p)$ is given by

$$\langle \mathcal{A} \rangle = \langle \mathcal{A} \rangle^{(0)} \frac{\sum_{n=0}^{\infty} [(-\beta)^n / n!] \langle \partial \mathcal{A} (\delta\mathcal{H})^n \rangle^{(0)} / \langle \mathcal{A} \rangle^{(0)}}{\sum_{n=0}^{\infty} [(-\beta)^n / n!] \langle (\delta\mathcal{H})^n \rangle^{(0)}} \quad (15a)$$

in which

$$\langle \mathcal{A} \rangle^{(0)} = \frac{\text{tr}\{\mathcal{A} \exp[-\beta(\mathcal{H}_0 - \mu\mathcal{N})]\}}{\text{tr}\{\exp[-\beta(\mathcal{H}_0 - \mu\mathcal{N})]\}}. \quad (15b)$$

The randomness of the overlayer is expressed by the fact that, for any physical quantities $\mathcal{A}_1, \mathcal{A}_2, \dots, \mathcal{A}_p$ depending on occupancy operators, we have $\langle \mathcal{A}_1 \mathcal{A}_2 \dots \mathcal{A}_p \rangle^{(0)} = \langle \mathcal{A}_1 \rangle^{(0)} \langle \mathcal{A}_2 \rangle^{(0)} \dots \langle \mathcal{A}_p \rangle^{(0)}$. In this case, the fraction in (15a) is one, $\langle \mathcal{A} \rangle = \langle \mathcal{A} \rangle^{(0)}$ and consequently the grand canonical average of \mathcal{A} can be indifferently calculated by using \mathcal{H} or \mathcal{H}_0 . Obviously, it is more convenient to use \mathcal{H}_0 , which amounts to abandoning the fluctuation Hamiltonian $\delta\mathcal{H}$. When a partial order exists in the overlayer, the fraction in (15a) is no longer exactly equal to one. In this case, the abandonment of $\delta\mathcal{H}$ and the replacement of $\langle n_i(p) \rangle$ with $\langle n_i(p) \rangle^{(0)}$ in (14b) is nothing other than the approximation called the molecular-field approximation (MFA). A simple examination of (14b) gives an obvious interpretation of \mathcal{H}_0 . Each site i occupied by adsorbate p interacts with three potentials: (i) $E_{\text{ads}}(p)$ describes its coupling with the substrate; (ii) $\mu_i(p)$ describes its coupling with a large reservoir containing molecules and atoms that are liable to be adsorbed (this reservoir is actually the world outside the adsorbate plus substrate complex); (iii) the molecular-field potential

$$V_i^{\text{MF}}(p) = \sum_{j,p'} U_{ij}(p, p') \langle n_j(p') \rangle \quad (16)$$

describes its coupling with the average potential created by molecules located at sites $j \neq i$.

Expression (16) shows that the molecular field at site i is expressed in terms of the average site occupancies $\langle n_j(p') \rangle$, which do not take account that site i is occupied by adsorbate p . If we want to calculate correlation functions credibly, we have necessarily to evaluate $V_i^{\text{MF}}(p)$ by replacing $\langle n_j(p') \rangle$ in (16) with $\langle n_j(p') \rangle_{ip}$ given in (12b). In this way, we introduce in our formalism the fact that site occupancies are correlated. To arrive at such a modified molecular-field approximation, the occupation operators $n_i(p)$ and $n_j(p')$, which occur in the interaction term of Hamiltonian (9), have to be decomposed into

$$n_i(p) = \langle n_i(p) \rangle_{ip} + \delta n_i^{ip}(p) \quad (17a)$$

$$n_j(p') = \langle n_j(p') \rangle_{ip} + \delta n_j^{ip}(p'). \quad (17b)$$

Henceforth, these expressions for $n_i(p)$ and $n_j(p')$ will replace the one given in (13). Then, putting back (17a) and (17b) into (9) and using relations (11) and (12a), \mathcal{H} and \mathcal{H}_0 now become

$$\mathcal{H} = \mathcal{H}_0 - \mu\mathcal{N} + \delta\mathcal{H} \quad (18a)$$

$$\begin{aligned} \mathcal{H}_0 - \mu\mathcal{N} = & - \sum_{i,p} \left(E_{\text{ads}}(p) + \mu_i(p) - \sum_{j,p'} U_{ij}^*(p, p') \langle n_j(p') \rangle \right) n_i(p) \\ & - \frac{1}{2} \sum_{i,p} \sum_{j,p'} U_{ij}^*(p, p') \langle n_i(p) n_j(p') \rangle \end{aligned} \quad (18b)$$

$$\delta\mathcal{H} = \frac{1}{2} \sum_{i,p} \sum_{j,p'} U_{ij}(p, p') \delta n_i^{ip}(p) \delta n_j^{ip}(p'). \quad (18c)$$

Let us examine the conditions for which we can abandon the quadratic term $\delta\mathcal{H}$ given by (18c). But first come back to the previous case where $\delta\mathcal{H}$ is given by (14c). In fact, the abandonment of this term requires that $\langle (\delta\mathcal{H})^n \rangle^{(0)}$ vanishes for any n . In the case $n = 1$, this condition means that $\langle \delta n_i(p) \delta n_j(p') \rangle = \Gamma_{ij}(p, p') = 0$ for any pair of distinct sites i and j . This occurs when the overlayer is totally disordered. Let us now consider the quadratic term $\delta\mathcal{H}$ given by (18c). A necessary condition to justify its abandonment is that

$$\langle \delta n_i^{ip}(p) \delta n_j^{ip}(p') \rangle = \Gamma_{ij}(p, p') \left(1 + \frac{\Gamma_{ij}(p, p')}{\langle n_i(p) \rangle \langle n_j(p') \rangle} \right) = 0. \quad (19)$$

This occurs either if there is no correlation between site occupancies (case already examined) or if $\Gamma_{ij}(p, p') = -\langle n_i(p) \rangle \langle n_j(p') \rangle$. This last condition can be rewritten in the form $\langle n_i(p) n_j(p') \rangle = 0$. Obviously, it cannot be fulfilled for any pair of different sites and any pair of adsorbates, otherwise we could only adsorb one adsorbate at one site of the surface. In practice, the quadratic term $\delta\mathcal{H}$ given by (18c) only involves pairs of indices that refer to nearest-neighbour, next-nearest-neighbour, third-nearest-neighbour sites at the very most. In effect, in many current cases, interaction between pairs of adsorbates is described by a very short-range potential. In this way, $\langle n_i(p) n_j(p') \rangle = 0$ only means that two adsorbates p and p' cannot coexist at nearest-neighbour, next-nearest-neighbour or third-nearest-neighbour sites. This situation occurs when the interaction potential between neighbouring adsorbates is repulsive and infinite. For this reason, condition (19) can never be verified exactly. What happens in practice is that, without being infinite, the nearest-neighbour potential is very large compared with $kT = 1/\beta$ and consequently the probability of finding a pair of adsorbates at two neighbouring sites is very much lower than the product of probabilities of finding them separately at each of these sites. Moreover, as we restrict ourselves here to small surface coverage, the

correlation function $\Gamma_{ij}(p, p')$, which is very close to $-\langle n_i(p) \rangle \langle n_j(p') \rangle$, is necessarily small. Finally, in the case of a surface *sparsely populated* with adsorbates interacting by a *short-range repulsive* potential, we can expect that the quadratic term $\delta\mathcal{H}$ given by (18c) can be neglected, even if this potential is large, which was not true in the MFA. Let us remark that the definition (8) of the grand canonical matrix allows us to add any constant to $\mathcal{H}_0 - \mu\mathcal{N}$ without changing the physical information contained in this matrix. So, for convenience, we can drop the last term in (18c). Finally, instead of using the Hamiltonian \mathcal{H} , we deal with

$$\mathcal{H}^{\text{SCMFA}} - \mu\mathcal{N} = \sum_{i,p} h_i^{\text{SCMFA}}(p) n_i(p) \quad (20a)$$

$$h_i^{\text{SCMFA}}(p) = -E_{\text{ads}}(p) - \mu_i(p) + \sum_{j,p'} U_{ij}^*(p, p') \langle n_j(p') \rangle_{\text{SCMFA}}. \quad (20b)$$

The index SCMFA indicates that this molecular-field approximation requires a self-consistent determination of $\Gamma_{ij}(p, p')$. The above Hamiltonian is a quasi-particle Hamiltonian. In particular, we can easily show that its average counts the interaction energy twice.

2.2. Determination of the site-occupancy pair correlation function

Neither MFA nor SCMFA allows one to calculate the site-occupancy pair correlation function by directly starting from its definition (6b). In fact, this calculation is carried out by using the well known fluctuation dissipation theorem:

$$\partial\langle A \rangle / \partial\mu_j(p') = \beta[\langle n_j(p') A \rangle - \langle n_j(p') \rangle \langle A \rangle] \quad (21)$$

in which A is a physical quantity that depends on site-occupancy operators $n_i(p)$. It allows one to give a relationship between the site-occupancy pair correlation function and the average site occupancies, between triplet and pair correlation functions, etc. For instance, in the case where $A = n_i(p)$, we obtain

$$\Gamma_{ij}(p, p') = (1/\beta) \partial\langle n_i(p) \rangle / \partial\mu_j(p'). \quad (22)$$

This expression will be used here to evaluate the pair correlation function. In a first stage, we have to determine the average occupation $\langle n_i(p) \rangle$. Using the expression (8) of the grand canonical density matrix in which \mathcal{H} is replaced by the expression (20a) of $\mathcal{H}^{\text{SCMFA}}$, we find

$$\langle n_i(p) \rangle = \frac{\exp[-\beta h_i(p)]}{\sum_{p_i=0}^{p_{\text{max}}} \exp[-\beta h_i(p_i)]}. \quad (23)$$

Index SCMFA has been abandoned for simplicity. Then, putting back (23) into (22) leads to

$$\Gamma_{ij}(p, p') = - \sum_{k,p_k} \Lambda_{ik}(p, p_k) \frac{\partial h_k(p_k)}{\partial\mu_j(p')} \quad (24a)$$

in which $\Lambda_{ik}(p, p_k)$ is given by

$$\Lambda_{ik}(p, p_k) = [\langle n_i(p) \rangle \delta_{pp_k} - \langle n_i(p) \rangle \langle n_i(p_k) \rangle] \delta_{ik}. \quad (24b)$$

The expression of $\partial h_k(p_k) / \partial\mu_j(p')$ occurring in (24a) can be evaluated from the SCMFA expression $h_k(p_k)$ given in (20b). Substitution of this expression into (24a) leads to

$$\Gamma_{ij}(p, p') = \sum_{k,p_k} \Lambda_{ik}(p, p_k) \left(\delta_{kj} \delta_{p_k p'} - \beta \sum_{l,p_l} U_{kl}^*(p_k, p_l) \Gamma_{lj}(p_l, p') - \sum_{l,p_l} \frac{\partial U_{kl}^*(p_k, p_l)}{\partial\mu_j(p')} \langle n_l(p_l) \rangle \right). \quad (25a)$$

All the difficulties in solving this equation come from its last term. Let us remark that the MFA amounts to replacing U^* with U . In this case, this term disappears together with these difficulties. Unfortunately, it must be emphasised that the MFA determination of Γ is paradoxical because it consists of evaluating correlation functions from average site occupancies, which have been obtained by assuming the absence of correlation! This inconsistency can lead to non-physical results such as negative values of $\langle n_i(p)n_j(p') \rangle$. To avoid this drawback without having to face the difficulties mentioned above, we shall neglect the third term in (25a). So, we implicitly assume that the renormalised potential U^* is independent of the chemical potential of sites. Let us now consider matrices Γ , Λ and \mathbf{U}^* whose coefficients are labelled with the pair of indices (i, p) by

$$(\Gamma)_{ip,ip'} = \Gamma_{ij}(p, p') \quad (26a)$$

$$(\Lambda)_{ip,ip'} = \Lambda_{ij}(p, p') \quad (26b)$$

$$(\mathbf{U}^*)_{ip,ip'} = U_{ij}^*(p, p'). \quad (26c)$$

With the above approximation, equation (25a) reduces to the form

$$\Gamma = \Lambda[\mathbf{1} - \beta\mathbf{U}^*\Gamma]. \quad (25b)$$

2.3. Determination of the structure factor

As seen in section 1, the structure factor $S(p, p', \mathbf{q})$ is given by

$$S(p, p', \mathbf{q}) = \sum_{i=1}^N \Gamma_{i1}(p, p') \exp(-i\mathbf{q}\mathbf{T}_i). \quad (27)$$

Here we have let $\mathbf{q} = \mathbf{k}_{\parallel} - \mathbf{k}_{\parallel}$. Conversely, we have the relation

$$\Gamma_{ij}(p, p') = \frac{1}{N} \sum_{\{\mathbf{q}\} \text{ in } B_1} S(p, p', \mathbf{q}) \exp[i\mathbf{q}(\mathbf{T}_i - \mathbf{T}_j)] \quad (28a)$$

or, when N becomes infinite,

$$\Gamma_{ij}(p, p') = \frac{A}{4\pi^2} \int_{B_1} d^2\mathbf{q} S(p, p', \mathbf{q}) \exp[i\mathbf{q}(\mathbf{T}_i - \mathbf{T}_j)]. \quad (28b)$$

In these expressions, B_1 is the first Brillouin zone in the 2D reciprocal lattice. In a similar way, we can define the Fourier transform of U^* :

$$\mathcal{U}^*(p, p', \mathbf{q}) = \sum_{i=1}^N U_{i1}^*(p, p') \exp(-i\mathbf{q}\mathbf{T}_i) \quad (29a)$$

and conversely

$$U_{ij}^*(p, p') = \frac{A}{4\pi^2} \int_{B_1} d^2\mathbf{q} \mathcal{U}^*(p, p', \mathbf{q}) \exp[i\mathbf{q}(\mathbf{T}_i - \mathbf{T}_j)]. \quad (29b)$$

Fourier transforms and inverse Fourier transforms are calculated by using the well known summation relations:

$$\begin{aligned} \sum_{i=1}^N \exp(-i\mathbf{q}\mathbf{T}_i) &= N\delta_{\mathbf{q},0} & \text{or} & & \sum_{i=1}^{\infty} \exp(-i\mathbf{q}\mathbf{T}_i) &= \frac{4\pi^2}{A} \delta(\mathbf{q}) \\ \frac{1}{N} \sum_{\{\mathbf{q}\} \text{ in } B_1} \exp[i\mathbf{q}(\mathbf{T}_i - \mathbf{T}_j)] &= \delta_{ij} & \text{or} & & \frac{A}{4\pi^2} \int_{B_1} d^2\mathbf{q} \exp[i\mathbf{q}(\mathbf{T}_i - \mathbf{T}_j)] &= \delta_{ij}. \end{aligned}$$

At this stage, we have to assume that $\mu_i(p)$ is independent of site i . Consequently, average occupancies $\langle n_i(p) \rangle$ become independent of sites. Then, using the above relations between correlation function, potential and their Fourier transform, it can easily be shown that the structure factor S obeys an equation that is very similar to equation (25b), which determines Γ . We obtain

$$\mathbf{S}(\mathbf{q}) = \Theta[1 - \beta \mathbf{u}^*(\mathbf{q})\mathbf{S}(\mathbf{q})]. \quad (30)$$

In this equation, the elements of matrices \mathbf{S} , Θ and \mathbf{u}^* depend on \mathbf{q} and are labelled with indices $p = 1, \dots, p_{\max}$. So, we have

$$\Theta_{pp'} = \langle n(p) \rangle \delta_{pp'} - \langle n(p) \rangle \langle n(p') \rangle \quad (31a)$$

$$(\mathbf{S}(\mathbf{q}))_{p,p'} = S(p, p', \mathbf{q}) \quad (31b)$$

$$(\mathbf{u}^*(\mathbf{q}))_{p,p'} = U^*(p, p', \mathbf{q}). \quad (31c)$$

An obvious solution of equation (30) is

$$\mathbf{S}(\mathbf{q}) = [1 + \beta \Theta \mathbf{u}^*(\mathbf{q})]^{-1} \Theta. \quad (32)$$

3. Case of binary chemisorption

3.1. Incoherent intensity

First, we consider the case where only one possible chemisorption state exists, that is to say where any chemisorption site can be occupied or not; hence the use of the word binary. As $p_{\max} = 1$, matrices Γ , Θ and \mathbf{u}^* in (32) reduce to scalars and the structure factor is given by

$$S(1, 1, \mathbf{q}) = \gamma(\mathbf{q}) = \frac{\langle n \rangle (1 - \langle n \rangle)}{1 + \beta \langle n \rangle (1 - \langle n \rangle) u^*(\mathbf{q})}. \quad (33)$$

In this way, expression (1) for the incoherent intensity becomes

$$I_{\text{incoh}}(\mathbf{k}_f^- \leftarrow \mathbf{k}_i^+) = \frac{4\pi^4 k_{f\perp}^2 k_{i\perp}^2}{A k_{i\perp} |K_{f\perp}|^2} \gamma(\mathbf{k}_{f\parallel} - \mathbf{k}_{i\parallel}) |K_1(1, \mathbf{k}_f^- \leftarrow \mathbf{k}_i^+)|^2 \quad (34)$$

that is to say a product of a form factor by a structure factor. Let us remark that, if the overlayer is sparsely populated, $\gamma(\mathbf{k}_{f\parallel} - \mathbf{k}_{i\parallel})$ is near $\langle n \rangle$ and consequently the incoherent intensity becomes proportional to the surface coverage in adatoms. In the present case, the structure factor $\gamma(\mathbf{k}_{f\parallel} - \mathbf{k}_{i\parallel})$ can be eliminated by using the Y function method mentioned in section 1.2. So, if we are only interested in the geometrical structure of the chemisorption site, then it is not necessary to know $\gamma(\mathbf{k}_{f\parallel} - \mathbf{k}_{i\parallel})$.

As previously noted in section 1, we can expect that diffuse LEED experiments allow us also to gain some information about the statistical distribution of adsorbates. In the present theory of diffuse LEED, this distribution is characterised by the site-occupancy pair correlation function $\Gamma_{ij}(p, p')$. This function has been evaluated by making a molecular-field approximation in which a renormalised pair interaction potential U^* has been introduced. In this way, this treatment is expected to be valid even if a strong repulsion between neighbouring atoms occurs. Such a situation is of great interest because it is liable to be found in a lot of experiments concerning the adsorption of light atoms such as chalcogens at the main single crystal surfaces of transition metals. In these cases, interaction between adatoms, which is essentially indirect, is all the more repulsive

as the number of substrate atoms that are adjacent to both adatoms is large (Lopez *et al* 1980, 1981). The order of magnitude of this nearest-neighbour indirect interaction can reach several hundred meV and is consequently large compared with kT at room temperature ($kT \approx 25$ meV). On the other hand, indirect interaction generally becomes less than kT as soon as adatoms are sufficiently distant to share no nearest-neighbour substrate atoms. Then, it may be repulsive or attractive (Einstein and Schrieffer 1973, Lopez *et al* 1980, 1981) and, in spite of its smallness, this pair interaction plays a role in the appearance of superstructures at very low temperature.

3.2. Validity of SCMFA in the binary chemisorption case

In section 2, we have implicitly assumed that the renormalised interaction potential U^* between adjacent adatoms remains finite even if the nearest-neighbour potential U becomes infinite. As a matter of fact, if we consider that neighbouring sites i and j are occupied by adsorbates p and p' and that the interaction potential $U_{ij}(p, p')$ tends to infinity, then $\Gamma_{ij}(p, p')$ tends to $-\langle n_i(p) \rangle \langle n_j(p') \rangle$ and consequently expression (11) for $U_{ij}^*(p, p')$ appears as a product of two factors in which one becomes infinite and the other vanishes. In the large-coupling limit, this product is totally indeterminate and we cannot assert *a priori* that $U_{ij}^*(p, p')$ tends to a finite value. Let us now carefully examine this problem in the case of binary chemisorption. For this purpose, we are going to establish an equation for U_{ij}^* that, contrarily to (11), does not depend on Γ_{ij} . In a first stage, we assume that ${}^0u^*(\mathbf{q})$ is small enough to expand the expression (33) of $\gamma(\mathbf{q})$ in a power series in $\langle n \rangle (1 - \langle n \rangle) \beta {}^0u^*(\mathbf{q})$. Then, using the fact that the inverse Fourier transform of $({}^0u^*(\mathbf{q}))^k$ for the lattice vector \mathbf{T}_i is the matrix product

$$(\mathbf{U}^*)_{i1}^k = \sum_{i_1} \sum_{i_2} \dots \sum_{i_{k-1}} \mathbf{U}_{ii_1}^* \mathbf{U}_{i_1 i_2}^* \dots \mathbf{U}_{i_{k-1} 1}^*$$

we calculate the inverse Fourier transform of this series and we obtain

$$\Gamma_{i1} = \langle n \rangle (1 - \langle n \rangle) \sum_{k=0}^{\infty} [-\beta \langle n \rangle (1 - \langle n \rangle)]^k (\mathbf{U}^*)_{i1}^k. \quad (35a)$$

As Γ_{i1} depends on the coefficients of the first column of the matrix $(\mathbf{U}^*)^k$, the k th-order term in (35a) is proportional to the number of possible ways that, starting from the reference site 1, we can arrive to site i by proceeding in k steps between nearest, next-nearest, . . . sites through the 2D surface lattice. Each of these possible ways defines a path. If we assume that U_{ij} is a nearest-neighbour interaction then we have

$$(\mathbf{U}^*)_{i1}^k = N(1, i, k) (U^*)^k$$

in which $N(1, i, k)$ is the number of possible distinct paths to travel from site 1 to site i by k steps between adjacent sites and U^* is the renormalised nearest-neighbour potential. The total number of paths in k steps is $(N_c)^k$ where N_c is the coordination number of a site (for example, $N_c = 4$ for a square lattice). In fact, as all paths with k steps have the same probability, $P(i, k) = N(1, i, k) / (N_c)^k$ is the probability of finding an adatom at site i after k steps, whereas this adatom was initially located at the reference site. Finally, in the particular case of a nearest-neighbour interaction, (35a) can be rewritten in the form

$$\Gamma_{i1} = \langle n \rangle (1 - \langle n \rangle) \sum_{k=0}^{\infty} P(i, k) [-\beta U^* N_c \langle n \rangle (1 - \langle n \rangle)]^k. \quad (35b)$$

Denoting by \mathbf{a} and \mathbf{b} the basis vectors of the 2D surface lattice, the i th lattice site associated

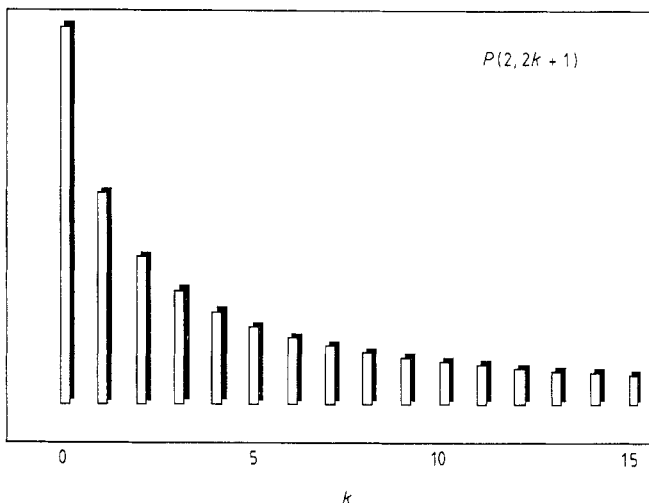


Figure 1. The first 15 terms of the sequence $P(2, 2k + 1)$ illustrate its convergence to 0 and show that the ratio of two consecutive terms approaches 1 ($P(2, 1) = 0.25$). It seems that this sequence decreases more slowly than $1/n$. In this case, the series $\sum P(2, 2k + 1)$ would diverge.

with the lattice vector $T_i = m_i a + n_i b$ is characterised by the pair of integers (m_i, n_i) . Then, let us define the parity of the i th site as $m_i + n_i$. In the case of a square lattice, it is easy to show that the parity of the number k of steps for travelling from the first site ($m_1 = 0, n_1 = 0$) to the i th site is identical to the parity of the latter. As a consequence, (35b) is an odd (respectively even) series if the i th site is odd (respectively even). On the other hand, we can travel through a triangular lattice from one site to another site by an odd or even number of steps. In fact, we have only to consider the infinite sequence of $P(i, k) \neq 0$. Then, when k tends to infinity, it is obvious that $P(i, k)$ approaches 0 and that the ratio $P(i, k)/P(i, k')$ of two consecutive terms approaches 1 (see figure 1). Then, use of the classical tests for convergence of series allows us to assert that a sufficient condition for obtaining the convergence of the above series is that

$$\beta U^* < \frac{1}{N_c \langle n \rangle (1 - \langle n \rangle)} \tag{35c}$$

The behaviour of the series (35b) for $\beta U^* = 1/[N_c \langle n \rangle (1 - \langle n \rangle)]$ can be determined only if we know in detail the sequence of $P(i, k)$, which is not the case. For a nearest-neighbour pair interaction, (11) shows that the evaluation of U^* requires knowledge of Γ_{21} . So, we particularly examine (35b) for $i = 2$ ($i = 2$ labels one of the neighbours of the reference site). If we assume that the series

$$\sum_{k=0}^{\infty} P(2, k)$$

converges to a constant C , then the correlation function $\Gamma_{21} = -C \langle n \rangle (1 - \langle n \rangle)$ for two adjacent sites is not close to $-\langle n \rangle^2$, as has been assumed previously (C only depends on the lattice geometry). This is *a fortiori* the case if the above series diverges. This means that the self-consistent determination of βU^* has necessarily to provide a value markedly less than $1/[N_c \langle n \rangle (1 - \langle n \rangle)]$.

Let us now examine whether this condition is verified in the particular case where U is a very strong repulsive nearest-neighbour potential. We first put back (35a) into (11) and we obtain the following equation for U^* :

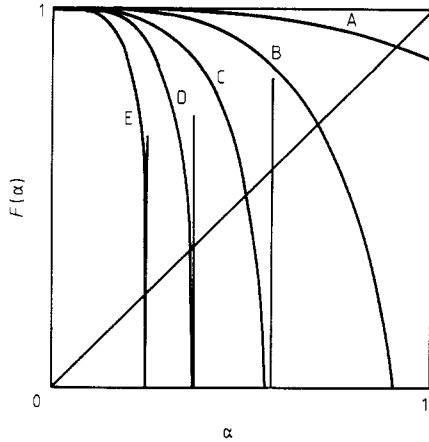


Figure 2. $F(\alpha)$ versus α is represented for different cases: curve A, $\langle n \rangle = 0.1$, $\alpha_0(\langle n \rangle) = 2.250$, $\alpha(\langle n \rangle) \approx 0.9$; curve B, $\langle n \rangle = 0.2$, $\alpha_0(\langle n \rangle) = 1$, $\alpha(\langle n \rangle) \approx 0.7$; curve C, $\langle n \rangle = 0.3$, $\alpha_0(\langle n \rangle) = 0.583$, $\alpha(\langle n \rangle) \approx 0.510$; curve D, $\langle n \rangle = 0.4$, $\alpha_0(\langle n \rangle) = 0.375$, $\alpha(\langle n \rangle) \approx 0.365$; curve E, $\langle n \rangle = 0.5$, $\alpha_0(\langle n \rangle) = 0.250$, $\alpha(\langle n \rangle) \approx 0.249$.

$$U^* = U \left(1 + \frac{1 - \langle n \rangle}{\langle n \rangle} \sum_{k=1}^{\infty} [-\beta \langle n \rangle (1 - \langle n \rangle)]^k (U^*)_{12}^k \right). \quad (36)$$

In this relation, summation over k runs from 1 instead of from 0 because $(U^*)_{12}^0$ is always 0. In fact, equation (36) has to be self-consistently solved together with those which determine the surface coverage $\langle n \rangle$:

$$h = -(E_{\text{ads}} + \mu) + \langle n \rangle \sum_k U_{1k}^* \quad (37a)$$

$$\langle n \rangle = \frac{\exp(-\beta h)}{1 + \exp(-\beta h)}. \quad (37b)$$

In the case of adatoms located at the sites of a 2D square lattice and interacting by a nearest-neighbour pair interaction, we can easily show that the renormalised coupling parameter U^* between adjacent adatoms is given by

$$\beta U^* = \frac{\beta U}{1 + \beta U (1 - \langle n \rangle)^2} \left(1 - \sum_{k=1}^{\infty} P(2, 2k + 1) \langle n \rangle^{2k} (1 - \langle n \rangle)^{2k+2} (\beta N_c U^*)^{2k+1} \right). \quad (38a)$$

As previously, the index $i = 2$ occurring in $P(2, 2k + 1)$ denotes one of the N_c sites that are adjacent to the reference site. This expression clearly shows that we have the inequalities

$$\beta U^* < \frac{\beta U}{1 + \beta U (1 - \langle n \rangle)^2} < \frac{1}{(1 - \langle n \rangle)^2}. \quad (38b)$$

In the strong-repulsive-coupling limit $\beta U \rightarrow \infty$, βU^* can be written in the form $\beta U^* = \alpha / (1 - \langle n \rangle)^2$ in which α is a dimensionless parameter. It follows from (38b) that $\alpha < 1$. This parameter is obtained by solving the equation:

$$\alpha = F(\alpha) = 1 - \alpha N_c \sum_{k=1}^{\infty} P(2, 2k + 1) \left(\frac{\alpha N_c \langle n \rangle}{1 - \langle n \rangle} \right)^{2k}. \quad (38c)$$

Figure 2 shows different solutions $\alpha(\langle n \rangle)$ of (38c) for different values of $\langle n \rangle$ and the values $\alpha_0(\langle n \rangle)$ for which $F(\alpha)$ diverges, that is to say

$$\alpha_0(\langle n \rangle) = (1 - \langle n \rangle) / N_c \langle n \rangle.$$

Let us come back to the condition (35c), which can be rewritten in the form

$\alpha(\langle n \rangle) < \alpha_0(\langle n \rangle)$. As previously noticed, $\alpha(\langle n \rangle)$ has actually to be markedly less than $\alpha_0(\langle n \rangle)$. Figure 1 shows that it is only true for small values of $\langle n \rangle$ ($\langle n \rangle \leq 0.2$). In the strong-coupling limit ($\beta U \rightarrow \infty$), expression (35b) for Γ_{i1} , which becomes

$$\Gamma_{i1} = \langle n \rangle (1 - \langle n \rangle) \sum_{k=0}^{\infty} P(i, k) \left(-\frac{\alpha(\langle n \rangle)}{\alpha_0(\langle n \rangle)} \right)^k \quad (39)$$

is expressed in terms of a series that quickly converges, provided that the coverage $\langle n \rangle$ is small. So, its inverse Fourier transform $\gamma(\mathbf{q})$ is a convergent series too. This justifies *a posteriori* that we can expand (33) in a power series.

3.3. Correlation functions at low surface coverage and their physical interpretation

For $\langle n \rangle \leq 0.2$, we can now provide a good approximation of Γ_{i1} by keeping only the lower-order terms of its expansion, even for large values of βU . We consider here the case of a square surface lattice. For convenience, in the present case we modify our notation in such a way that Γ_{mn} represents the correlation function between occupancies of the reference site and of the site defined by the lattice vector $m\mathbf{a} + n\mathbf{b}$. From (35a) and (38a), we easily obtain the following results:

$$\Gamma_{10} \approx \frac{-\beta U \langle n \rangle^2 (1 - \langle n \rangle)^2}{1 + \beta U (1 - \langle n \rangle)^2} \quad (40a)$$

$$\Gamma_{11} \approx \frac{2\beta^2 U^2 \langle n \rangle^3 (1 - \langle n \rangle)^3}{[1 + \beta U (1 - \langle n \rangle)^2]^2} \approx 2\Gamma_{20} \quad (40b)$$

$$\Gamma_{21} \approx \frac{-3\beta^3 U^3 \langle n \rangle^4 (1 - \langle n \rangle)^4}{[1 + U(1 - \langle n \rangle)^2]^3} \approx 3\Gamma_{30} \quad (40c)$$

$$\Gamma_{22} \approx \frac{6\beta^4 U^4 \langle n \rangle^5 (1 - \langle n \rangle)^5}{[1 + \beta U (1 - \langle n \rangle)^2]^4} \approx \frac{3}{2}\Gamma_{31} \approx 6\Gamma_{40}. \quad (40d)$$

In the strong-repulsive-coupling limit, (40a) indicates that Γ_{10} approaches $-\langle n \rangle^2$ or equivalently that the probability $\langle n_{00}n_{10} \rangle$ of finding two adjacent adatoms is of order greater than 2 in $\langle n \rangle$. So, at low coverage two adatoms cannot coexist at adjacent sites if they interact by a strong repulsive potential. Expressions (40b–d) show that, if sites (m, n) and $(0, 0)$ are not adjacent, then Γ_{mn} is of order greater than 2 in $\langle n \rangle$. It follows that $\langle n_{00}n_{mn} \rangle \sim \langle n \rangle^2$, which means that occupancies of non-adjacent sites are very weakly correlated. Examination of (40a–d) allows us also to remark that the sign of Γ_{mn} is directly related to the parity of $m + n$. More precisely, if an adatom is adsorbed at the origin site then, in its vicinity, the sublattice corresponding to $m + n$ even is occupied more than the odd sublattice. Such a result indicates a trend in the appearance of a $c(2 \times 2)$ superstructure. The appearance of a $p(2 \times 2)$ superstructure would be similarly predicted by incorporating the next-nearest-neighbour interactions. So far, we have assumed that U is positive. The previous developments are still valid if U is negative provided that it is small in modulus compared with kT . In this case, expressions (40a–d) indicate that Γ_{mn} is always slightly positive. It means that if the reference site is occupied, then occupancies of the first-, second-, third-, . . . nearest-neighbour sites are slightly larger than the average site occupancy. So, for small negative pair interaction potentials, there is a trend towards condensation in the vicinity of an occupied site.

3.4. Diffuse LEED from vacancies

We cannot end this section without noting that $S(1, 1, \mathbf{q})$ only depends on $\langle n \rangle(1 - \langle n \rangle)$. This remark suggests that the expressions (33) for the structure factor and (34) for the

incoherent intensity remain valid when $\langle n \rangle$ is near 1, which corresponds to an almost complete top layer. This situation has been examined by Rous and Pendry (1985) when surface and bulk atoms are identical. These authors give a multiple scattering theory of diffuse LEED from isolated surface vacancies. They conclude that the diffuse LEED intensity is proportional to the form factor of an isolated surface atom and they investigate this form factor by using the Y function method. As a site of the surface is either occupied or not by one kind of atom, the incoherent intensity has the form given in (1) for $p_{\max} = 1$ (Le Bossé *et al* 1988), that is to say the form of expression (34). In this way, the diffuse LEED intensity can be investigated with the help of the Y function method.

Nevertheless, even in this situation, it would be interesting to obtain some information about the structure factor. Since the expression for $S(1, 1, \mathbf{q})$ given in (33) can be used only if the condition (19) is satisfied, we have to reconsider the validity of this condition in the case of an almost complete top layer. For this purpose, it will be convenient to deal with the vacancy occupation operator $n_i(0) = 1 - n_i(1)$ rather than with $n_i(1)$. It is easy to show that

$$\Gamma_{ij}(0, 0) = \Gamma_{ij}(1, 1) = \langle n_i(0)n_j(0) \rangle - \langle n_i(0) \rangle \langle n_j(0) \rangle.$$

So, p and p' can be replaced by 0 in (19). As previously seen in section 2.1, this relation is fulfilled either if there is no correlation between site occupancies or if $\Gamma_{ij}(1, 1) = \Gamma_{ij}(0, 0) = -\langle n_i(0) \rangle \langle n_j(0) \rangle$ for a pair of neighbouring sites i and j . The last condition is actually equivalent to $\langle n_i(0)n_j(0) \rangle = 0$ and means that two vacancies cannot be found at a pair of neighbouring sites. This would imply the existence of a short-range repulsive potential between them. However, by replacing $n_i(1)$ with $1 - n_i(0)$ in the pseudo-Hamiltonian (9), it is easy to show that the pair interaction potential between surface atoms is identical to that between vacancies. As a matter of fact, the cohesion of the crystal surface requires these potentials to be attractive. This result is not surprising if we note that the number of bonds we have to break to create two adjacent vacancies is less than for creating two separated vacancies. As a consequence, vacancies tend to condense and the effects of this condensation are probably the creation or the displacement of steps and kinks. Then, we can legitimately ask if, in realistic situations, the diffuse LEED intensity comes from surface defects such as steps and kinks rather than vacancies? In fact, attraction between vacancies contradicts the condition $\Gamma_{ij}(0, 0) = -\langle n_i(0) \rangle \langle n_j(0) \rangle$ and the only way to satisfy condition (19) is to assume that there is no correlation between site occupancies ($\Gamma_{ij}(0, 0) = 0$), that is to say that vacancies are randomly distributed. Such a situation is liable to be observed at a temperature sufficiently high to have the interaction potential small compared with kT . In this case we have

$$\Gamma_{j1}(1, 1) = [n_v(1 - n_v)]\delta_{j1}.$$

This expression, which depends on the vacancy concentration $n_v = 1 - \langle n \rangle$, allows us to deduce $S(1, 1, \mathbf{k}_{\parallel} - \mathbf{k}_{\parallel})$ from (6b) and I_{incoh} from (1):

$$I_{\text{incoh}}(\mathbf{k}_f^- \leftarrow \mathbf{k}_i^+) = \frac{4\pi^4 k}{A k_{i\perp}} \frac{k_{f\perp}^2}{|K_{f\perp}|^2} n_v(1 - n_v) |K_1(\mathbf{k}_f^- \leftarrow \mathbf{k}_i^+)|^2.$$

Finally, as $n_v(1 - n_v) = \langle n \rangle(1 - \langle n \rangle)$, this expression is identical to the limit of the expression (34) when $\langle n \rangle$ approaches 1. So, in agreement with Rous and Pendry (1985), the diffuse LEED intensity coming from vacancies is proportional to the form factor of a single surface atom. However, contrarily to the case of a surface layer sparsely populated with adatoms, the multiple scattering processes inside an almost complete surface layer

play an important role. In this way, the expression for K_1 given in (3a) has to be replaced by the general expression (4.14) given in I.

4. Case where two chemisorption states exist

In this section, we examine two situations for which $p_{\max} = 2$. In the first situation, a quasi-complete layer contains two kinds of atom, which occupy well defined sites of the surface lattice. For instance, this situation corresponds to disordered metallic binary alloys for which all surface sites are not necessarily occupied. So, a small concentration in vacancies is taken into account. In the second situation one kind of molecule is adsorbed at two equivalent sites. Both chemisorption states associated with both chemisorption sites are assumed to be statistically equivalent.

4.1. Case of a quasi-complete surface atomic layer composed of two kinds of atom

Let us call the atoms of the surface atomic layer A and B. Instead of dealing with $\langle n(A) \rangle$ and $\langle n(B) \rangle$, it is more convenient to consider the two independent parameters c_A and ε given by

$$c_A = \frac{\langle n(A) \rangle}{\langle n(A) \rangle + \langle n(B) \rangle} \quad (41a)$$

$$\varepsilon = 1 - \langle n(A) \rangle - \langle n(B) \rangle. \quad (41b)$$

We assume that the overlayer is almost complete. In this way, the parameter ε is small compared with 1. Actually, the incoherence of the wave scattered at the surface comes from the chemical disorder inside the top layer as well as the chemical disorder of deeper atomic layers. So, neglecting the latter can seem to be an unrealistic situation. However, recent LEED experiments (Baudoing *et al* 1986) on Pt–Ni alloys indicate that, in some particular cases (for instance, the (111) single-crystal surface of Pt10–Ni90 alloy), the second atomic layer practically contains only one kind of atom ($\approx 100\%$ Ni) and thus is not chemically disordered. In this way, this layer contributes weakly to the incoherence of the scattered wave. On the other hand, incoherence due to the chemical disorder inside the bulk of the alloy could be ascribed to the third, fourth, etc, atomic layers from the surface. However, their contribution to incoherent intensities is actually negligible because twice their distance from the surface is near to or more than the inelastic mean free path at diffuse LEED energies. In this particular case, we can conclude that the incoherent intensity essentially comes from the disorder inside the surface atomic layer.

Using (41a) and (41b), it is easy to show that the matrix Θ defined in (31a) can be decomposed into

$$\Theta = c_A(1 - c_A)\mathbf{V} + \delta\Theta \quad (42a)$$

in which \mathbf{V} is the symmetrical matrix

$$\mathbf{V} = \begin{bmatrix} 1 & -1 \\ -1 & 1 \end{bmatrix} \quad (42b)$$

whose coefficients are labelled by A and B, and $\delta\Theta$ is a matrix that vanishes with the vacancy concentration ε . Let us substitute the expression (42a) for Θ into (32). Then, we obtain

$$\mathbf{S}(q) = c_A(1 - c_A)\mathbf{V} + \delta\Theta - \beta c_A(1 - c_A)\mathbf{V}\mathbf{Q}^*(q)\mathbf{S}(q) - \beta\delta\Theta\mathbf{Q}^*(q)\mathbf{S}(q) \quad (43a)$$

in which $\mathbf{Q}^*(q)$ is given by

$$\mathbf{u}^*(\mathbf{q}) = \begin{bmatrix} \mathcal{U}^*(A, A, \mathbf{q}) & \mathcal{U}^*(A, B, \mathbf{q}) \\ \mathcal{U}^*(B, A, \mathbf{q}) & \mathcal{U}^*(B, B, \mathbf{q}) \end{bmatrix}. \quad (43b)$$

4.1.1. *Case of a complete top layer.* First, let us examine the case of a complete surface layer. Parameter ε vanishes and equation (43a) reduces to

$$\mathbf{S}_0(\mathbf{q}) = c_A(1 - c_A)\mathbf{V}[1 - \beta\mathbf{u}^*(\mathbf{q})\mathbf{S}_0(\mathbf{q})] \quad (44)$$

which can be solved exactly. For this purpose, we first have to establish the following identity:

$$[1 + \beta c_A(1 - c_A)\mathbf{V}\mathbf{u}^*(\mathbf{q})]^{-1} = 1 - \beta\gamma_0(\mathbf{q})\mathbf{V}\mathbf{u}^*(\mathbf{q}). \quad (45)$$

This expression depends on $\gamma_0(\mathbf{q})$ given by

$$\gamma_0(\mathbf{q}) = \frac{c_A(1 - c_A)}{1 + \beta c_A(1 - c_A)\mathcal{V}^*(\mathbf{q})} \quad (46)$$

in which $\mathcal{V}^*(\mathbf{q})$ is defined as

$$\mathcal{V}^*(\mathbf{q}) = \mathcal{U}^*(A, A, \mathbf{q}) + \mathcal{U}^*(B, B, \mathbf{q}) - 2\mathcal{U}^*(A, B, \mathbf{q}). \quad (47)$$

Use of the above identity in equation (44) leads to

$$\mathbf{S}_0(\mathbf{q}) = \gamma_0(\mathbf{q})\mathbf{V}. \quad (48)$$

Examination of (33) and (46) shows a certain similarity between binary chemisorption and the present case. This is not surprising because for a complete surface layer consisting of two kinds of atom, we find again an alternative between two occupation states: sites are occupied by A or B (instead of being occupied or unoccupied). However, the physical situations corresponding to the pair atom A/atom B and to the pair adatom/vacancy are very different. First, interactions between atoms A or between atoms B are considered in the same way, whereas no interaction between vacancies occurs. Consequently, it does not matter whether we consider case $c_A \approx 0$ or case $c_B \approx 0$ whereas cases $\langle n \rangle \approx 0$ and $\langle n \rangle \approx 1$ are not equivalent (see discussion in section 3.4). Secondly, the interaction potential between atoms of an alloy generally has an attractive short-range part whereas the indirect interaction between neighbouring adatoms is mostly repulsive. In fact, expression (47) shows that the statistical distribution of atoms a and B depends on the effective potential

$$V_{ij}^* = U_{ij}^*(A, A) + U_{ij}^*(B, B) - 2U_{ij}^*(A, B). \quad (49)$$

In order to simplify the discussion, let us assume that $U_{ij}^*(p, p')$ is a nearest-neighbour interaction potential. If the average of potentials between identical atoms is exactly equal to the potential between two different atoms, then $V_{ij}^* = 0$ and we obtain from relations (28a) and (48)

$$\Gamma_{ij}(p, p') = c_A c_B V(p, p')\delta_{ij}. \quad (50)$$

This correlation function describes the case of a totally disordered surface layer. On the other hand, when $V^* > 0$, the average attraction between A and B is stronger than the attraction between identical atoms. Atoms A and B tend to be surrounded by unlike neighbours. In the opposite case, when $V^* < 0$, the same kind of atoms tend to clump together. It must be emphasised that such a trend to segregation inside the top layer is certainly closely connected to the catalytic activity of surface alloys inasmuch as binding sites with one kind of atom are more often present than binding sites with unlike atoms.

Now let us come back to condition (19). As previously mentioned, this condition only concerns pairs of sites that are very close together. Before writing it, we can establish from (28b), (48) and (42b) that

$$\Gamma_{ij}(\mathbf{A}, \mathbf{A}) = \Gamma_{ij}(\mathbf{B}, \mathbf{B}) = -\Gamma_{ij}(\mathbf{A}, \mathbf{B}) = \Gamma_{ij}. \quad (51)$$

In this way, condition (19) is rewritten in the form

$$\Gamma_{ij}(1 + \Gamma_{ij}/c_A^2) \simeq 0 \quad (52a)$$

$$\Gamma_{ij}(1 + \Gamma_{ij}/c_B^2) \simeq 0 \quad (52b)$$

$$\Gamma_{ij}(1 - \Gamma_{ij}/c_A c_B) \simeq 0. \quad (52c)$$

If Γ_{ij} is not small compared with 1, (19) reduces to three incompatible conditions $\Gamma_{ij} \simeq -c_A^2$, $\Gamma_{ij} \simeq -c_B^2$ and $\Gamma_{ij} \simeq c_A c_B$. Consequently, the SCMFA, which consists of neglecting the quadratic term of \mathcal{H} in fluctuation occupations, is valid if Γ_{ij} is small and $\gamma_0(\mathbf{q})$ too. This requires a small effective potential V^* compared with kT and a low concentration in one of the elements of the alloy.

From (48) and (1) we now calculate the incoherent intensity. However, let us note that, in the present case, coherent multiple scattering inside the top layer plays an important role and thus we can no longer use the expression (3a) of K_1 : we must revert to the expression (4.14) of K_1 given in I. This calculation leads to the expression

$$I_{\text{incoh}}^{(0)}(\mathbf{k}_i^- \leftarrow \mathbf{k}_i^+) = \frac{4\pi^4}{A k_{i\perp}} \frac{k_{i\perp}^2}{|K_{i\perp}|^2} \gamma_0(\mathbf{k}_{i\parallel} - \mathbf{k}_{i\parallel}) |K_1(\mathbf{A}, \mathbf{k}_i^- \leftarrow \mathbf{k}_i^+) - K_1(\mathbf{B}, \mathbf{k}_i^- \leftarrow \mathbf{k}_i^+)|^2 \quad (53)$$

in which the superscript (0) refers to the case $\varepsilon = 0$. For reasons examined above, this incoherent intensity is very similar to that obtained in the case of binary chemisorption (see (34)). However, let us remark that the form factor is the square modulus of the difference between the effective transition matrix of each atom of the alloy. The Y function method can again be applied here to investigate the diffuse LEED intensities without having to consider the structure factor $\gamma_0(\mathbf{q})$. However, if this method allows us to gain information about the position of surface atoms relative to the atoms of the second layer, we cannot obtain any information about their statistical distribution. Such information is contained in the structure factor $\gamma_0(\mathbf{q})$ and can only be drawn from direct comparison between measured and calculated intensities.

4.1.2. Case of an incomplete top layer. As a matter of fact, investigation of the form factor by using the Y function method is no longer possible for a top layer composed of two kinds of atoms and containing vacancies. Let us now treat this situation in the specific case where the concentration ε of vacancies is small. For this purpose let us separate $\mathbf{S}(\mathbf{q})$ into two terms,

$$\mathbf{S}(\mathbf{q}) = \mathbf{S}_0(\mathbf{q}) + \delta\mathbf{S}(\mathbf{q}). \quad (54)$$

From equations (43a) and (48), we obtain an equation for $\delta\mathbf{S}$:

$$[1 + \beta c_A(1 - c_A)\mathbf{V}\mathbf{q}^*(\mathbf{q})]\delta\mathbf{S}(\mathbf{q}) = \delta\Theta[1 - \beta\gamma_0(\mathbf{q})\mathbf{q}^*(\mathbf{q})\mathbf{V}] - \beta\delta\Theta\mathbf{q}^*(\mathbf{q})\delta\mathbf{S}(\mathbf{q}). \quad (55)$$

As we want a first-order expression in ε of $\delta\mathbf{S}(\mathbf{q})$, we neglect the last term in (55). Again using identity (45), we easily solve (55) and we obtain

$$\delta\mathbf{S}(\mathbf{q}) = [1 - \beta\gamma_0(\mathbf{q})\mathbf{V}\mathbf{q}^*(\mathbf{q})]\delta\Theta[1 - \beta\gamma_0(\mathbf{q})\mathbf{q}^*(\mathbf{q})\mathbf{V}]. \quad (56)$$

In this expression, $\delta\Theta$ derived from (31a) and (42a) is given by

$$\delta\Theta = \varepsilon \begin{bmatrix} -c_A(1 - 2c_A) & 2c_A(1 - c_A) \\ 2c_A(1 - c_A) & (1 - c_A)(1 - 2c_A) \end{bmatrix}. \quad (57)$$

Then, putting back (56) and (54) into (1), we obtain an expression for the incoherent intensity, which is the sum of two terms,

$$I_{\text{incoh}} = I_{\text{incoh}}^{(0)} + \delta I_{\text{incoh}}. \quad (58)$$

The first term associated with the complete top layer is given by (53) and the second term is proportional to the vacancy concentration ε . For convenience, let us define

$$H_1(\text{A}, \mathbf{k}_f^- \leftarrow \mathbf{k}_i^+) = \{1 - \beta\gamma_0(\mathbf{q})[\mathcal{U}^*(\text{A}, \text{A}, \mathbf{q}) - \mathcal{U}^*(\text{A}, \text{B}, \mathbf{q})]\}K_1(\text{A}, \mathbf{k}_f^- \leftarrow \mathbf{k}_i^+) \\ + \beta\gamma_0(\mathbf{q})[\mathcal{U}^*(\text{A}, \text{A}, \mathbf{q}) - \mathcal{U}^*(\text{A}, \text{B}, \mathbf{q})]K_1(\text{B}, \mathbf{k}_f^- \leftarrow \mathbf{k}_i^+) \quad (59a)$$

$$H_1(\text{B}, \mathbf{k}_f^- \leftarrow \mathbf{k}_i^+) = \beta\gamma_0(\mathbf{q})[\mathcal{U}^*(\text{B}, \text{B}, \mathbf{q}) - \mathcal{U}^*(\text{A}, \text{B}, \mathbf{q})]K_1(\text{A}, \mathbf{k}_f^- \leftarrow \mathbf{k}_i^+) \\ + \{1 - \beta\gamma_0(\mathbf{q})[\mathcal{U}^*(\text{B}, \text{B}, \mathbf{q}) - \mathcal{U}^*(\text{A}, \text{B}, \mathbf{q})]\}K_1(\text{B}, \mathbf{k}_f^- \leftarrow \mathbf{k}_i^+). \quad (59b)$$

In these relations we have let $\mathbf{q} = \mathbf{k}_{f\parallel} - \mathbf{k}_{i\parallel}$. Finally, δI_{incoh} is given by

$$\delta I_{\text{incoh}} = \frac{4\pi^4 k}{Ak_{i\perp}} \varepsilon \frac{k_{f\perp}^2}{K_{f\perp}^2} \{-c_A(1 - 2c_A)|H_1(\text{A})|^2 + (1 - c_A)(1 - 2c_A)|H_1(\text{B})|^2 \\ + 2c_A(1 - c_A)[H_1(\text{A})\overline{H_1(\text{B})} + \overline{H_1(\text{A})}H_1(\text{B})]\}. \quad (60)$$

Expressions (59) and (60) show that, in the case where $\varepsilon \neq 0$, a calculation of incoherent intensity requires knowledge of all pair interaction potentials. At this stage, let us note that the description of interactions between atoms of a disordered alloy in terms of pair interactions has recently been proved in a paper by Treglia *et al* (1988). More precisely it has been shown that an effective Ising model can be used to study ordering at transition-metal alloy surfaces. In fact, Hamiltonian (9) used here for $p_{\text{max}} = 2$ and $\langle n(0) \rangle = 0$ could also be rewritten in the form of an Ising Hamiltonian. Moreover, in this paper, an effective pair interaction potential is evaluated for the three low-index faces of the FCC lattice as a function of the average d band filling and of the concentration c_A . This potential turns out to be very complicated. It cannot be approximated by a nearest-neighbour and next-nearest-neighbour potential as in the case of chemisorption of light atoms. So, evaluation of diffuse LEED intensities in the case of an incomplete layer is certainly a tricky problem.

4.2. Case of a loosely populated overlayer

We consider now two occupation states u and v and we assume that $\langle n(u) \rangle + \langle n(v) \rangle$ is small compared with 1. For example, u and v may denote two possible non-equivalent chemisorption sites for one kind of atom or molecule, or two kinds of atom or molecule each of which may be adsorbed at a well defined chemisorption site. Now, the expression of the structure factor obtained from (32) is no longer as simple as in the binary chemisorption case. Let us assume that coverages $\langle n(u) \rangle$ and $\langle n(v) \rangle$ and the renormalised potential $\beta^0 \mathcal{U}^*(p, p', \mathbf{q})$ are such that the coefficients of the matrix $\beta^0 \Theta \mathcal{U}^*(\mathbf{q})$ remain small compared with 1. Similarly to the case of binary chemisorption, we can expand (32) in a power series of these coefficients. However, we only keep terms of first and second order

in $\langle n(u) \rangle$ and $\langle n(v) \rangle$, which leads to the following approximation of the structure factor $S(\mathbf{q})$:

$$S(p, p', \mathbf{q}) \approx \langle n(p) \rangle \delta_{pp'} - \langle n(p) \rangle \langle n(p') \rangle [1 + \beta^0 u^*(p, p', \mathbf{q})]. \quad (61)$$

Let us first examine the validity of this approximation. From (61) and (28a), we can derive an approximate expression of the correlation function:

$$\Gamma_{ij}(p, p') \approx [\langle n(p) \rangle \delta_{pp'} - \langle n(p) \rangle \langle n(p') \rangle] \delta_{ij} - \beta \langle n(p) \rangle \langle n(p') \rangle U_{ij}^*(p, p'). \quad (62)$$

Use of this expression in (11) leads to the renormalised potential

$$U_{ij}^*(p, p') \approx \frac{U_{ij}(p, p')}{1 + \beta U_{ij}(p, p')}. \quad (63)$$

In this way, condition (19) becomes

$$\frac{\langle n(p) \rangle \langle n(p') \rangle \beta U_{ij}(p, p')}{[1 + \beta U_{ij}(p, p')]^2} = 0. \quad (64)$$

As $U_{ij}(p, p')$ is a short-range order potential, we can restrict condition (64) to the case where i and j are adjacent sites. So, at low coverage, this condition is roughly fulfilled for any repulsive interaction potentials or for attractive potentials that are small compared with kT (in the latter case $\Gamma_{ij}(p, p')$ almost cancels). We have here similar restrictions to those previously obtained in the binary chemisorption case.

Using (61) and the general expression (1) for the incoherent intensity, we get the following approximation of I_{incoh} :

$$\begin{aligned} I_{\text{incoh}}(\mathbf{k}_f^- \leftarrow \mathbf{k}_i^+) &= \frac{4\pi^4 k}{A k_{i\perp}} \frac{K_{f\perp}^2}{|K_{f\perp}|^2} \left(\langle n(u) \rangle |K_1(u, \mathbf{k}_f^- \leftarrow \mathbf{k}_i^+)|^2 + \langle n(v) \rangle |K_1(v, \mathbf{k}_f^- \leftarrow \mathbf{k}_i^+)|^2 \right. \\ &\quad - |\langle n(u) \rangle K_1(u, \mathbf{k}_f^- \leftarrow \mathbf{k}_i^+) + \langle n(v) \rangle K_1(v, \mathbf{k}_f^- \leftarrow \mathbf{k}_i^+)|^2 \\ &\quad - \beta \sum_{p, p'=u, v} \langle n(p) \rangle \overline{K_1}(p, \mathbf{k}_f^- \leftarrow \mathbf{k}_i^+) \\ &\quad \left. \times {}^0 u^*(p, p', \mathbf{k}_{f\parallel} - \mathbf{k}_{i\parallel}) \langle n(p') \rangle K_1(p', \mathbf{k}_f^- \leftarrow \mathbf{k}_i^+) \right). \end{aligned} \quad (65)$$

In the case where the matrix coefficients $\beta^0 u^*(p, p', \mathbf{q})$ are about 1, we cannot neglect the last term in expression (65), which is associated with the presence of a partial order inside the overlayer. Then, it can easily be seen that the logarithmic derivative L of the incoherent intensity with respect to incident energy at constant $\mathbf{k}_{f\parallel} - \mathbf{k}_{i\parallel}$ (and consequently the Y function) depends not only on the form factors $K_1(u)$ and $K_1(v)$ but also on $\beta^0 u^*(p, p', \mathbf{q})$, that is to say on the statistical distribution of occupied states. In this case, the use of this method is meaningless. Conversely, in the case of a random distribution of occupied states ($\beta^0 u^*(p, p', \mathbf{q}) \approx 0$), the last term in (65) can be neglected. Then, the question of the elimination of a structure factor no longer arises. In this case, the use of the Y function method amounts to taking another look at the experimental data without modifying the physical information that we can draw from them.

Let us remark that, in the limit of very low surface coverage, the first two terms in expression (65) play a predominant role. For comparison, let us come back to the expression (34) of the diffuse LEED intensity obtained for one adsorbate and calculated in this limit:

$$I_{\text{incoh}}(\mathbf{k}_f^- \leftarrow \mathbf{k}_i^+) \approx \frac{4\pi^4 k}{A k_{i\perp}} \frac{k_{f\perp}^2}{|K_{f\perp}|^2} \langle n \rangle |K_1(1, \mathbf{k}_f^- \leftarrow \mathbf{k}_i^+)|^2.$$

Then, the first two terms in (65) can be interpreted as the sum of incoherent intensities associated with each scatterer separately. Unfortunately, diffuse LEED experiments cannot be carried out for very small surface coverage because: (i) measurement of incoherent intensities becomes tricky; (ii) geometrical disorder in the substrate and chemical disorder in the overlayer are liable to exert an equal influence on the incoherence of waves scattered at the surface. Consequently, available and usable experimental data probably include surface coverages for which one cannot keep only the first two terms in expression (65). In fact, it can easily be seen that, when the surface coverage reaches 0.2, the third term in this expression is liable to be important if interferences between waves emitted at the two kinds of scatterers are constructive, which can occur for certain values of k_{\parallel}^{-} and k_{\parallel}^{+} . So, even in the case of a totally random overlayer, the incoherent intensity does not generally reduce to the average of incoherent intensities associated with each adsorbed species.

In fact, the Y function method has been applied to cases where there are two or more than two kinds of bonding sites. For instance, Blackman *et al* (1988) use a Y function analysis for CO/Pt(1 1 1), from which it is concluded that, at one-third of a monolayer coverage at 160 K, $(88 \pm 5)\%$ of the CO molecules occupy top sites and $(12 \pm 5)\%$ bridge sites. First, let us note that, in this case, there are four possible different bonding sites at least: a top bonding site ($p = t$), a bridge bonding site ($p = b_1$) and two others ($p = b_2$ and $p = b_3$) obtained by rotations by 120° . In this way, the expression (65) for the incoherent intensity is no longer valid and has to be replaced by a similar expression including four states t , b_1 , b_2 and b_3 instead of two states u and v . Blackman *et al* (1988) assume that 'diffuse LEED intensities due to adsorbates at different bonding sites can simply be added incoherently'. In this case, the incoherent intensity would have the form

$$I_{\text{incoh}} = \frac{4\pi^4 k}{A k_{i\perp}} \frac{k_{f\perp}^2}{|K_{f\perp}|^2} \left(\langle n(t) \rangle |K_1(t)|^2 + \sum_{i=1}^3 \langle n(b_i) \rangle |K_1(b_i)|^2 \right) \quad (66)$$

which means that a term similar to the third term in (65) would be negligible. As previously mentioned, this approximation, which is good at very low coverage, may be questionable in the present case, where the total coverage in CO is about 0.3. Moreover, use of the Y function method *a priori* assumes that the true expression of the diffuse LEED intensity is obtained by multiplying (66) by a structure factor, which is not actually the case (see (65)). In fact, no factorisation of the first two terms of (65) can be achieved with another factor only depending on $k_{\parallel} - k_{\parallel}$. Blackman *et al* (1988) notice that the R factor value of 0.55 is not as good as that found in the O/W(001) structure analysis, $R = 0.13$ (Heinz *et al* 1986). This is not surprising because the adsorption of oxygen at the W(001) surface is a binary chemisorption case where the Y function method can be used, while it is not the case for the CO/Pt(1 1 1) system. In this last case, diffuse LEED intensities have to be calculated by taking into account short-range coupling between CO molecules located at two neighbouring sites. Then, these calculated intensities must be directly compared with measured intensities.

The Y function method has also been used to investigate the diffuse LEED spectrum obtained from the CO₂/Ni(110) system, which is not relevant to the binary chemisorption case (Illing *et al* 1988). A lot of possible bonding sites are examined (hollow, short bridge, long bridge and top sites) and for each of them two non-equivalent directions parallel and perpendicular to the $\langle 110 \rangle$ azimuth are considered. Among all the possible situations that can be envisaged, the authors sort on the top site for which both orthogonal directions are equally occupied: it definitely leads to the best R factor ($R \approx$

0.15 instead of $R \approx 0.2\text{--}0.3$ for other situations). Thus, we should be in the case $p_{\max} = 2$. For each distinct chemisorption site, two parameters are considered: the CO bond angle and the C–Ni distance. In this way, the best agreement between experiment and theory corresponds to a minimum of the R factor in a four-dimensional parameter space. Three spatial configurations of the CO₂ molecules are considered: they lead to three sets of optimal parameters. Unfortunately, the R factors calculated for these three sets are very near. In this way, no conclusions about the spatial configuration of the CO₂ molecule have been drawn. The authors conclude that a larger set of experimental data would allow them to distinguish between the three adsorption geometries.

Assuming that we have the top bonding site with two possible directions, we think that steric interactions absolutely prevent certain configurations with two molecules adsorbed at neighbouring sites. This short-range interaction is very strong, in such a way that the last term in (65) cannot be neglected. So, the use of the Y function method is not suitable in this case. For reasons previously mentioned, the third term in (65) can be a non-negligible correction to the first two. Its relative importance depends on the coverage in CO₂, which is not indicated in this paper. At this stage, let us remark that the R factor value obtained in this case (0.15–0.17) is close to that obtained for the O/W(001) case and is markedly better than in the CO/Pt(111) case. This fact could appear as a point in favour of the use of the Y function method. However, we can ask about the meaning of an R factor obtained from one diffuse LEED spectrum. In fact, the answer to this question is in a paper by Starke *et al* (1988) in which the misleading nature of conclusions resulting from the use of only one Y function screen is pointed out. Paraphrasing these authors, we can state that an accurate surface structure determination of a complex involving elements such as substrate reconstructions, low-symmetry adsorbate positions or perhaps one involving molecular adsorbates requires the use of several diffuse LEED spectra. In conclusion, for this case, it should be advisable to compare experiment and theory by using (i) a database as large as possible and (ii) a diffuse LEED theory including the statistical distribution of molecules inside the overlayer.

5. Conclusion and discussion

The increasing importance of partially or imperfectly ordered chemisorbed overlayers requires a very serious surface structure analysis. Diffuse LEED is a powerful tool for achieving such an analysis. So far, this technique has mainly been used for determining the geometry of a *unique* binding site, which can be occupied or not (binary chemisorption). In this case, *and only in this case*, the incoherent intensity reduces to the product of a form factor, which only depends on the binding site geometry, and a structure factor, which characterises the statistical distribution of occupied sites. Then, using the fact that the structure factor depends only on the difference between components parallel to the surface of initial and final wavevectors, it is possible to exhibit a function (Pendry's Y function) of the form factor only. So, the binding site geometry can be investigated without having to treat the statistical aspects of the diffuse LEED problem. In the case where several species are co-adsorbed or where one adsorbed species has several possible binding sites, the use of the Y function method is meaningless. For low surface coverages and high temperatures, interactions between adsorbates do not dictate the position of one adsorbed species with respect to another. Then, we can consider that adsorbates are randomly distributed on the surface and consequently no structure exists. For this reason, we are not faced with the elimination of a structure factor: direct com-

parison of measured and calculated diffuse LEED intensities allows us to reach the geometry of binding sites. Unfortunately, available experimental data correspond to surface coverages that have to be large enough to ascribe the incoherence of the scattered wave mainly to disorder in the overlayer. For such coverages, we can express serious doubts about the randomness of the overlayer: then, evaluation of diffuse LEED intensities actually requires the determination of site-occupancy pair correlation functions as well as their Fourier transforms. Finally, except for the binary chemisorption case, diffuse LEED studies have necessarily to be carried out by directly comparing measured and calculated intensities. So, geometry of binding sites and statistical distribution of adsorbed species on these sites need to be considered together to carry out these calculations.

In fact, the statistical aspects of the diffuse LEED problem have practical and theoretical importance for surface catalysis. For instance, it may be important to know if two adsorbed species are more frequently located at neighbouring sites than at distant sites, or if binding sites of a binary alloy surface are compounded with one kind of atom rather than several. A molecular-field treatment of diffuse LEED in which correlations are introduced allows one to evaluate the structure factor for a large variety of situations, including binary chemisorption. Because of its relative simplicity, we have particularly focused on the latter. We have shown that we can obtain a fairly good description of overlayers sparsely populated with repulsive adsorbates. This description remains valid if the pair interaction potential U between two adjacent adatoms is very large compared with kT , provided that the surface coverage is small ($\langle n \rangle < 0.2$ for a square lattice). Beyond this limit, we can imagine that diffuse LEED intensities drop abruptly to zero while the appearance of fractional order peaks in the LEED pattern is evidence of long-range order inside the overlayer (diffuse LEED intensities concentrate into new LEED channels). In fact, we are only interested here in the first stages of the appearance of order. By varying the temperature and exposure of a single-crystal surface to a gas, we can expect that a good description of the increasing appearance of order that can be observed in diffuse LEED experiments allows one to go back from the effect to the cause, that is to give the interaction force law between adsorbates.

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