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MONTE CARLO SIMULATION OF PARTIALLY ORDERED ATOMIC LAYERS ADSORBED ON THE MONOCRISTALLINE SURFACES

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The calculations of the correlations functions and structure factors are performed by means of the Monte Carlo simulation. The results for O/Ni(001) system are presented and compared with those obtained using self-consistent molecular field approximation and cumulant expansion method. The simulation for more complex system CO/Pt(111) is also performed. The calculations of the topological correlations allow us to find the coverage dependence of the incoherent scattering amplitude which can be experimentally detected.

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1. Introduction

1.1. Outline of the diffuse low-energy electron diffraction problems

For a couple of decades one of the most developed branches of research works is the surface science. According to new technologies and computer possibilities many phenomena are known much better now, however, some new problems have been arisen in this way. The problem of friction is one of the best examples [1, 2]. Now, a new approach to this problem from the atomic point of view is a basis for the cooperation of mechanicians and physicists, although these two fields have been distinguished up to the moment.

The only way to understand complexity of the surface phenomena is to know point by point what is going on there, what are the real values of representative parameters, what kind of structures appears there and what kind of phenomena plays the most important role at contact points, in adsorbed layers and so on. The experiments using atomic force microscopes or dealing with diffuse low-energy electron diffraction (LEED) are the most sensitive between other techniques [3, 4].

The latter has attracted our attention recently and some of the statistical aspects of diffuse LEED has been reported in the previous papers [5, 6]. Earlier, Le Bossé et al. [7] gave a general expression of the incoherent intensity of electrons backscattered at a single crystal surface partially covered with a disordered overlayer

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

where

$$S(p, p', k_{f\parallel} - k_{i\parallel}) = \sum_{j=1}^N \Gamma_{0j}(p, p') \exp[-i(k_{f\parallel} - k_{i\parallel})T_j] \quad (2)$$

is the Fourier transform of the site-occupancy pair correlation function $\Gamma_{0j}(p, p')$ which is defined on the substrate surface lattice as follows:

$$\Gamma_{0j}(p, p') = \langle n_0(p)n_j(p') \rangle - \langle n_0(p) \rangle \langle n_j(p') \rangle. \quad (3)$$

For other details see [5, 8, 9]. As usually the averages in (3) are performed over a grand canonical ensemble

$$\langle A \rangle = \text{tr}\{\rho A\} = \frac{\text{tr}\{\exp[-\beta(H - \mu N)A]\}}{\text{tr}\{\exp[-\beta(H - \mu N)A]\}} \quad (4)$$

and a Hamiltonian H of adsorbate-substrate and adsorbate-adsorbate interactions is following:

$$H - \mu N = - \sum_{i=1}^N [E_{\text{ads}} + \mu_i] n_i + \frac{1}{2} \sum_{i,j=1}^N U_{ij} n_i n_j. \quad (5)$$

It is important to notice that the magnitude of pair interaction potential U_{ij} in (5) as well as its sign is responsible for the crystalline structure of adsorbed layer even in the nearest-neighbour approximation. It has been shown using different approaches described below [10]. For O/Ni(001) system with strong repulsive interactions and coverages $\theta < 0.25$ it is only possible to obtain $c(2 \times 2)$ superstructure instead of $p(2 \times 2)$ one. The latter case can be generated using next nearest and farther neighbour approximation in Monte Carlo simulation what is described in Sec. 2.

1.2. Theoretical approach to statistical aspects of diffuse LEED problem

Up to now, site-site correlation functions (3) have been calculated using two approximated methods [10]: the self-consistent molecular field approximation (SCMFA) and cumulant expansion method (CEM). Then, it is possible to determine structure factors (2) in some restricted cases: low coverage limit or weak interaction potentials in (5). The SCMFA method gives the following approximated expressions for the coverage θ and for the infinite number of correlation functions Γ_{mn} :

$$\theta = \frac{1}{1 + \exp[\beta(-E_{\text{ads}} - \mu + 4U^*\theta)]}, \quad (6)$$

$$[1 - \beta\theta(1 - \theta)U^*] \Gamma_{10} + \beta\theta(1 - \theta)U^*(2\Gamma_{11} + \Gamma_{20}) = -\beta\theta^2(1 - \theta)^2U^*, \quad (7)$$

$$\Gamma_{mn} + \beta\theta(1 - \theta)U^*(\Gamma_{m-1n} + \Gamma_{m+1n} + \Gamma_{mn-1} + \Gamma_{mn+1}) = 0, \quad (8)$$

where U^* is the renormalized interaction potential, θ is surface coverage and $\beta = (k_B T)^{-1}$.

The second approach (CEM) at the first stage using Dirac's δ -function method [11] gives the exact expressions for mean occupation $\langle n_1 \rangle$ and for "pure" correlation function $\langle n_1 n_j \rangle$ [12]

$$\langle n_1 \rangle = A_1 + A_2 \sum_i \langle n_i \rangle + A_3 \sum'_{i,j} \langle n_i n_j \rangle + A_4 \sum'_{i,j,k} \langle n_i n_j n_k \rangle + A_5 \langle n_2 n_3 n_4 n_5 \rangle, \quad (9)$$

$$\begin{aligned} \langle n_1 n_m \rangle &= A_1 \langle n_m \rangle + A_2 \sum_i \langle n_i n_m \rangle + A_3 \sum'_{i,j} \langle n_i n_j n_m \rangle \\ &+ A_4 \sum'_{i,j,k} \langle n_i n_j n_k n_m \rangle + A_5 \langle n_2 n_3 n_4 n_5 n_m \rangle, \end{aligned} \quad (10)$$

where coefficients A_k are the known functions of temperature parameter β and interaction potential U for s.q. substrate structure in the nearest neighbour approximation. Then, using the following cumulant expansion for multi-correlations in (10):

$$\langle n_1 \rangle = \theta, \quad (11)$$

$$\langle n_1 n_2 \rangle = \Gamma_{12} + \theta^2, \quad (12)$$

$$\langle n_1 n_2 n_3 \rangle = \{n_1 n_2 n_3\} + \theta(\Gamma_{12} + \Gamma_{13} + \Gamma_{23}) + \theta^3, \quad (13)$$

$$\begin{aligned} \langle n_1 n_2 n_3 n_4 \rangle &= \{n_1 n_2 n_3 n_4\} + (\Gamma_{12}\Gamma_{24} + \Gamma_{13}\Gamma_{24} + \Gamma_{14}\Gamma_{23}) \\ &+ \theta(\{n_1 n_2 n_3\} + \{n_1 n_2 n_4\} + \{n_1 n_3 n_4\} + \{n_2 n_3 n_4\}) \\ &+ \theta^2(\Gamma_{12} + \Gamma_{13} + \Gamma_{14} + \Gamma_{23} + \Gamma_{24} + \Gamma_{34}) + \theta^4 \end{aligned} \quad (14)$$

and neglecting cumulants $\{n_1 n_2 \dots n_k\}$ of the order k higher than 2 the system (9)-(10) is transformed into the approximated expressions for the coverage θ and correlation functions Γ_{mn} [13]

$$\begin{aligned} \theta &= A_1 + 4A_2\theta + 6A_3\theta^2 + 4A_4\theta^3 + A_5\theta^4 + (2A_3 + 4A_4\theta)(2\Gamma_{11} + \Gamma_{20}) \\ &+ a_5(2\Gamma_{11}^2 + \Gamma_{20}^2), \end{aligned} \quad (15)$$

$$\Gamma_{10} + \theta(1 - \theta)K_1(\theta)(2\Gamma_{11} + \Gamma_{20}) = H_1(\theta), \quad (16)$$

$$\Gamma_{mn} + K_1(\theta)(\Gamma_{m-1n} + \Gamma_{m+1n} + \Gamma_{mn-1} + \Gamma_{mn+1}) = 0, \quad (17)$$

$$H_1(\theta) = A_2 + A_3(1 + \theta) + A_4\theta(3 - 2\theta) + 2A_5\theta^2(1 - \theta), \quad (18)$$

$$K_1(\theta) = -[A_2 + 3A_3\theta + 3A_4\theta^2 + A_5\theta^3]. \quad (19)$$

These two methods give the reliable results only for very low coverages and weak interactions between adsorbates in nearest neighbour approximation. To extend investigations of diffuse LEED statistical aspects for arbitrary parameter region and more complicated systems we are obliged to perform the simplest Monte Carlo simulation of adlayer.

2. Monte Carlo simulation of adsorbed layer O/Ni(001) and CO/Pt(111)

The object of this Monte Carlo simulation is to provide estimation of the statistical mechanical Boltzmann averages of site-site pair occupation correlation functions (3) of the adsorbed gas atoms or molecules onto certain substrate surface as O/Ni(001) or CO/Pt(111). To obtain a Markov chain of representative configurations C_i with energy E_i we perform a biased random walk in the phase space called the importance sampling [14]. The transition probabilities for any local change of single adatom position is determined as usually in the following way:

$$P_{i \rightarrow i+1} = \begin{cases} \exp(-\beta|E_{i+1} - E_i|) & \text{for } E_{i+1} > E_i, \\ 1 & \text{for } E_{i+1} \leq E_i. \end{cases} \quad (20)$$

For any configuration C_i which consists of many local adatom changes (practically it is a number of adatoms taken into consideration) it is easy to calculate temporary mean value, namely

$$\bar{\Gamma}_{mn}(t) = \frac{1}{\text{TOTAL}} \sum \Gamma_{mn}(t), \quad (21)$$

where the summation is performed over all simultaneously occupied adatom posi-

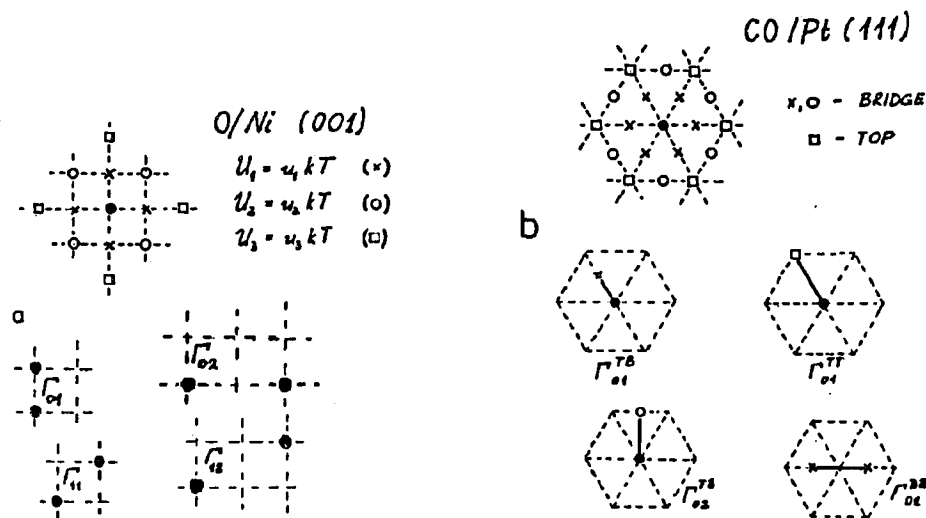


Fig. 1. Suggested model for simulation of statistical distribution of (a) oxygen adatoms on Ni(001) substrate; (b) carbon-oxide admolecules on Pt(111) substrate with different interaction energies u_1 , u_2 and u_3 . Below pairs of correlated adatoms are shown contributing to (a) Γ_{ij} and (b) Γ_{ij}^s ($r, s = \text{TOP, BRIDGE}$) pair correlation functions (32).

tions of a given type (mn) — see Fig. 1. TOTAL denotes the number of all possible pairs (mn) (occupied or not) on the adlayer in question. Hence, we obtain mean value of parameter $\Gamma_{mn}(t)$ along the Markov chain of the length L

$$\Gamma_{mn} \equiv \langle \bar{\Gamma}_{mn} \rangle_{M-C} = \frac{1}{L} \sum_{t=N_0}^{N_0+L} \langle \bar{\Gamma}_{mn}(t) \rangle. \tag{22}$$

In (22) the summation is started with the configuration C_{N_0} which is chosen in such a way that the contribution of initial configuration C_0 in the ensemble is finally lost. This configuration is generated by adding adatoms onto the substrate sites chosen randomly but its final occupation is according to probability (20) which can be written in the following form to shorten this procedure:

$$P_+ \propto \exp(-\Delta n_1 u_1 - \Delta n_2 u_2 + \Delta n_3 u_3), \tag{23}$$

where Δn_i is a number of created i -bonds with energy $U_i = u_i k_B T$, $i = 1, 2, 3$, respectively (compare Fig. 1).

As usually dealing with a pseudo-random number generator we should be very careful to get right results especially close to the critical regions where the systems become very sensitive and unstable [15] and correlation length can be comparable with the linear size N of the simulated mesh. For this reason the number of different characteristics is checked, namely "time" variation of particular Markov processes in Fig. 2 or their distances $L^2(t)$ for too small mesh compared with the biggest piece of 160000 sites (Fig. 3).

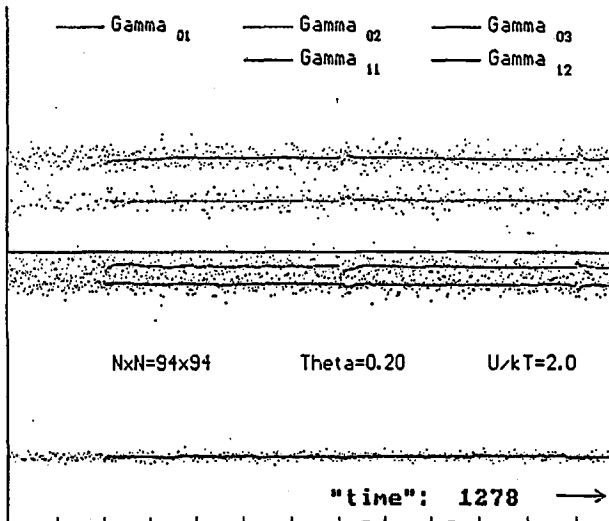


Fig. 2. Artificial time evolution of certain Markov process for O/Ni(001) system with n.n. approximation and $u_1 = 2.0$; $\theta = 0.2$. Drops denote temporary values of respective correlation functions (33), solid lines represent mean values recalculated every $t = 500$ configurations to get coarse grained type averaging with $N_0 = 200$.

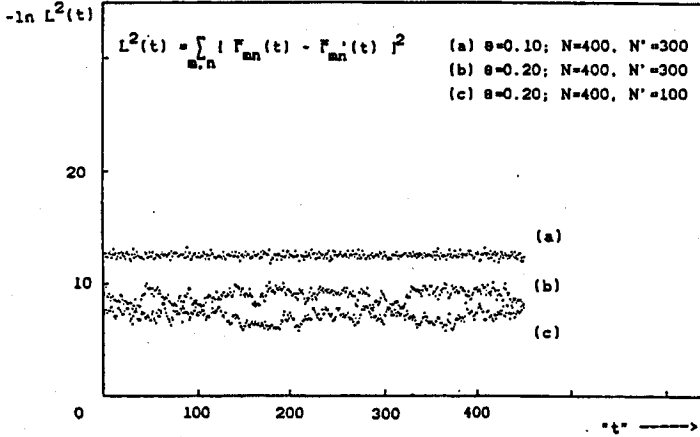


Fig. 3. Distance $L^2(t)$ of different Markov chains vs. "time" for different sizes N' compared with the biggest simulated piece $N \times N = 400 \times 400$ when $\theta = 0.10$ and 0.20 , respectively.

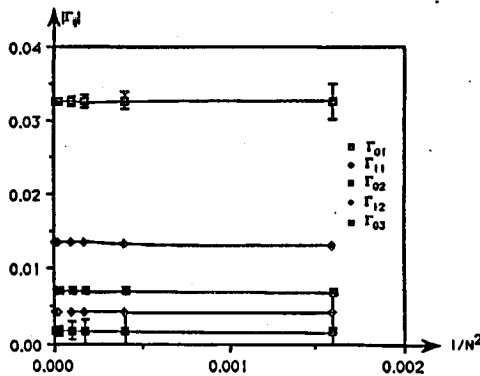


Fig. 4. Pair correlation function Γ_{ij} of adsorbed partially ordered layer O/Ni(001) for $\theta = 0.20$ and $u_1 = 2.0$ (n.n. approx.) with periodic boundary conditions plotted vs. inverse square dimension of the lattice. Left hand side results show the good tendency to thermodynamic limit for $N \rightarrow \infty$ and $\theta = \text{const.}$

In order to omit the final size problems we perform a linear extrapolation of the correlation functions Γ_{ij} versus N^{-2} for $N \rightarrow \infty$. It is worth noticing that for usual diffuse LEED parameters, outside of the critical regions, this procedure is not needed, see Fig. 4.

As it was told before, a sufficient number of local changes with probability (20) is performed to close any configuration C_t , therefore there is no problem with correlation of successive configurations. However, it should be verified carefully whether the slowing down close to the critical region $\theta \rightarrow \theta_{\text{crit}}$ allows one to ob-

tain reliable results after reliable time of simulations. For that reason the different lengths L of the representative Markov chain are considered together with the averaging procedure of coarse grained type (22), where the mean values for different parts of Markov process (Fig. 2) are compared. Then, if they are reasonable stable over an extended number of coarse grained averages we consider this value to be the ensemble average of the correlation function in question.

It should be noticed that the presented simulation is performed not to generate realistic physical adsorption-desorption process observed during the LEED experiment. In order to describe the statistical distribution of adatoms at the substrate surface in question we can perform averaging procedure (22) dealing only with the representative subset of canonical ensemble of configurations $\{C_t\}_{\text{can}}$.

3. Conclusions and final remarks

Two theoretical methods SCMFA and CEM reviewed above give the similar infinite set of linear algebraic equations for which solutions Γ_{mn} are close to those obtained by Monte Carlo simulations only for a certain restricted area: (1) if potential interaction is rather weak compared with kT , $0 < \theta < \theta_{\text{crit}}$; (2) for any potential interaction but in the low coverage limit $\theta < 0.05$ (see Fig. 5 and 6).

The closer to θ_{crit} the greater number of bigger islands of well-defined superstructures occurs, therefore the only Monte Carlo simulation results are correct (see Fig. 7a-d).

It is worth noticing that the more the system is free (for small coverage) the more configurations could be achieved (the smaller determination of successive M-C configurations C_t) and it means the bigger fluctuations of the resulting parameters $\Gamma_{mn}(t)$ — compare the plot for $\theta = 0.1$ with the rest of the results in Fig. 6.

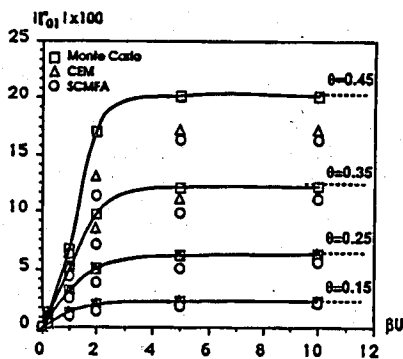


Fig. 5. The strongest pair correlation function Γ_{01} plotted vs. interaction energy parameter βU for different coverages $\theta = 0.15, 0.25, 0.35$ and 0.45 according to three presented methods. The dash line represents the asymptotic value of θ^2 .

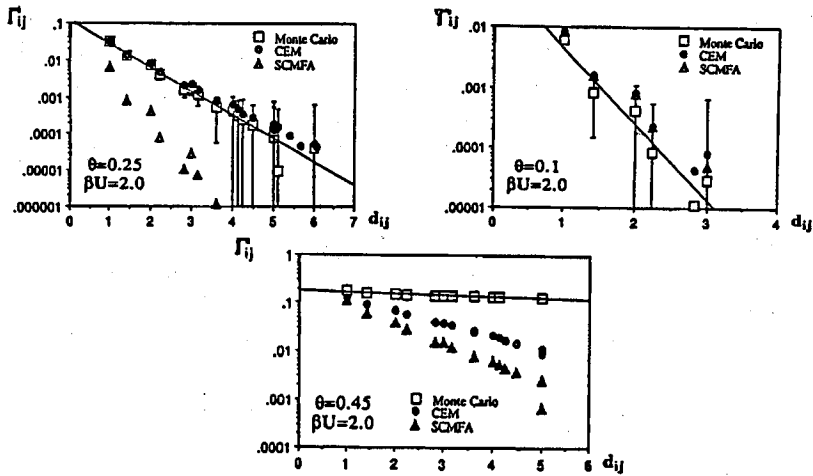


Fig. 6. Pair correlation function Γ_{ij} vs. distance of correlated adatoms d_{ij} for repulsive interaction of adjacent sites $u_1 = 2.0$ and various coverages $\theta = 0.1, 0.25$ and 0.45 . Solid line represents the exponential decay of correlations with a distance.

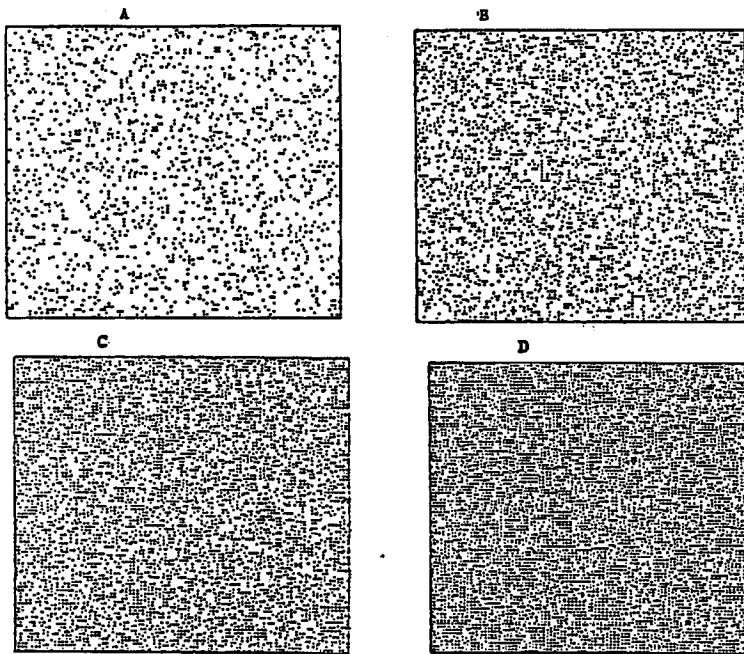


Fig. 7. Snapshot pictures of a system O/Ni(001) with interactions $u_1 = 10.0, u_2 = 2.5$ and $u_3 = -0.5$ for $N \times N = 179 \times 179$ and different coverages (a) $\theta = 0.05$, (b) $\theta = 0.10$, (c) $\theta = 0.15$ and (d) $\theta = 0.20$.

Finally, increasing the coverage parameter θ from the diffuse LEED region to the classical one we can observe the contribution of the structure factor of the system to the LEED pattern, especially just below the critical region when $p(2 \times 2)$ superstructure islands start to grow up. This feature is shown in Fig. 8 where for successive coverages θ in the case of O/Ni(001) system one can observe the presence of sharp structures near fractional order peaks which is essential for the diffuse LEED experiment.

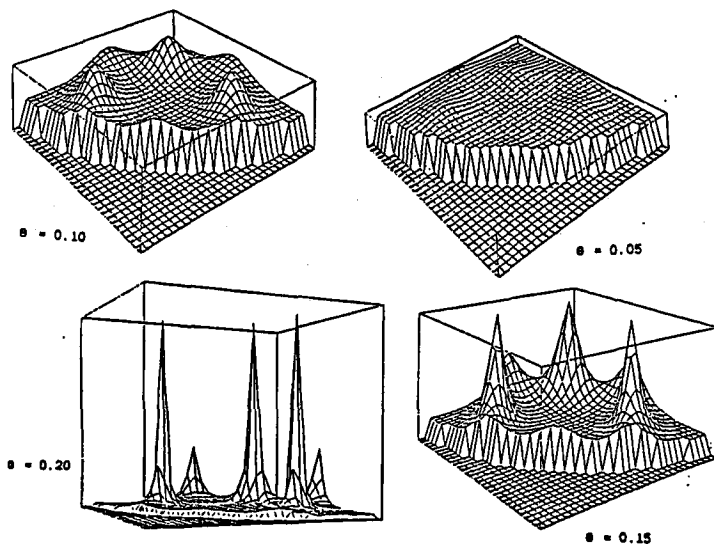


Fig. 8. Perspective representation of the structure factor $S(q)$ for the system O/Ni(001) as in Fig. 7; $U_1 = 10k_B T$, $U_2 = 2.5k_B T$, $U_3 = -0.5k_B T$.

From the other hand, the diffuse LEED intensity obtained via the structure factor $S(q)$ for the case of more than one kind of chemisorption sites like CO/Pt(111) system [6] is not tractable with the use of the Y function method contrary to the suggestion of Saldin et al. [16]. The extension of our previous simulations to the second case of CO/Pt(111)-system (see Fig. 1b) allowed us to obtain the snapshots of adsorbed carbon-monoxide molecules. Because we have obtained the proper superstructure islands known from other experiments, so we can conclude that the comparison experience/theory should take into consideration the contribution of structure factor $S(q)$. The final proof is the task for the next paper in progress as the continuation of the just presented results for CO/Pt(111) simulation.

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