

INFLUENCE OF CHEMISORBED ATOMS ON SURFACE VIBRATIONS. II

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The surface vibrations of a square lattice with chemisorbed atoms are studied in terms of the occupation numbers and correlation functions. For two kinds of chemisorbed atoms and for various value of gas pressure the surface frequencies are calculated using for (n) and (m) different approximations. The absorption isotherms, the coverage and the correlation function as functions of T are given as well.

ВЛИЯНИЕ ХЕМОСОРБИРОВАННЫХ АТОМОВ НА ПОВЕРХНОСТНЫЕ КОЛЕБАНИЯ-II

В работе изучаются поверхностные колебания квадратной решетки с хемосорбированными атомами при помощи чисел заполнения и корреляционных функций. При использовании для (n) и (m) различных приближений были рассчитаны частоты поверхностных колебаний для двух видов хемосорбированных атомов и для различных значений давления газа. Определены также зависимость изотерм поглощения, покрытия и корреляционных функций от температуры T .

1. INTRODUCTION

It is now a well-established fact that the adatom-adatom interaction is an important factor determining many aspects of thermodynamic and kinetic properties of crystal surfaces with chemisorbed species. This is most clearly demonstrated by the tendency of chemisorbed layers to form distinct phases which possess well-defined two-dimensional periodicity and order [1]. Recently, considerable attention has been devoted to experimental observations and calculations of superstructures of two-dimensional surface lattices with adsorbate and to transitions between different phases [2]. In these calculations the lattice gas approximation has been used which assumes the rigidity of the underlying substrate [3, 4, 5]. This approximation was shown to describe satisfactorily experimental results in

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many cases. On the other hand the adsorbate-induced reconstruction, e.g. in the case of adsorbed hydrogen on tungsten (100) shows the necessity to involve both adsorbate and substrate into the calculation [6]. The strong dependence of properties of the adsorbed gas and of the substrate on the state of its counterpart leads to interesting effects also in kinetics where it is responsible, e.g. for an oscillatory behaviour of CO oxidation on Pt [7].

The purpose of our paper is to calculate the influence of chemisorbed atoms with lateral interactions upon the vibrational spectra of surface substrate atoms and the effect of dynamical properties of the substrate on the thermodynamic properties of adsorbed lattice gas.

In our calculations we use a simple model simulating the properties of (100) crystal surfaces with chemisorbed atoms. We replace the surface substrate layer by a quadratic two-dimensional harmonic square lattice. In both substrate and adsorbate we assume nearest neighbour interactions only. The method of calculation based on the Bogolyubov variational principle and quasicheical, polynomial and mean field approximations for lattice gas of adsorbed molecules was developed in detail in [8].

II. MODEL HAMILTONIAN

The adsorbing surface of a solid is modelled by a monatomic two-dimensional lattice. Each adsorbed atom (adatom) is assumed to be strongly bound to one surface atom. In this case the system surface + adatoms can be described by the Hamiltonian

$$H = \sum_i \frac{P_i^2}{2(M+mn_i)} + \frac{1}{2} \sum_{i,j} \Phi(\mathbf{R}_i - \mathbf{R}_j) + \nu \sum_i n_i + \frac{1}{2} \sum_{i,j} J(\mathbf{R}_i - \mathbf{R}_j) n_i n_j \quad (1)$$

where M and m are the masses of the surface atoms and of the adatoms, respectively. P_i are their momenta. The interaction between the two surface atoms located at the lattice sites i, j is described by the potential $\Phi(\mathbf{R}_i - \mathbf{R}_j)$ depending on the position vectors $\mathbf{R}_i, \mathbf{R}_j$. The potential $J(\mathbf{R}_i - \mathbf{R}_j)$ has the same meaning as $\Phi(\mathbf{R}_i - \mathbf{R}_j)$, but in the system of adsorbed atoms. $n_i = 0, 1$ are the occupation number operators and ν is the effective chemical potential of adatoms. These are considered in thermodynamical equilibrium with an ideal monatomic gas of low pressure. Therefore $\nu = -(\epsilon + \mu_g)$ where ϵ has the meaning of the energy of adsorption and μ_g is the chemical potential

$$\mu_g = kT \ln \left[\frac{P}{(kT)^{5/2}} \left(\frac{2\pi h^2}{m} \right)^{3/2} \right].$$

Here P is the pressure of the gas, m is the mass of gas atoms and T is temperature.

Now, using the Bogolyubov variational method, we introduce the model Hamiltonian

$$H = H_{ph} + H_{ad} \quad (2)$$

$$H_{ph} = \sum_k \frac{P_k^2}{2M_0} + \frac{1}{4} \sum_{\alpha, \beta} A_{ik}^{\alpha\beta} X_{ik}^{\alpha} X_{ik}^{\beta}$$

$$\mathbf{R}_k = \langle \mathbf{R}_k \rangle + u_k, \quad X_{ik}^{\alpha} = u_i^{\alpha} - u_k^{\alpha}$$

$$H_{ad} = \nu_0 \sum_i n_i + \frac{1}{2} \kappa \sum_{i,j} n_i n_j$$

in which the surface atom variables and the adatom variables are separated. The dynamics of surface atoms is described by H_{ph} . Here, as it is usually in lattice dynamics the potential energy expands around the equilibrium positions $\langle \mathbf{R}_k \rangle$ and only the first non-zero terms are considered. The adatoms are described by the Hamiltonian H_{ad} , which can be transformed easily into the known Ising Hamiltonian. The variational parameters are determined by the minimum of the thermodynamical potential with respect to $M_0, A_{ik}^{\alpha\beta}, \nu_0$ and κ . These conditions yield [8].

$$A_{ik}^{\alpha\beta} = \nu_0^{\alpha} \nabla_i^{\alpha} \langle \Phi(\mathbf{R}_i - \mathbf{R}_j) \rangle_{ph} + \langle n_i n_j \rangle_{ad} \nabla_i^{\alpha} \nabla_j^{\beta} \langle J(\mathbf{R}_i - \mathbf{R}_j) \rangle_{ph}$$

$$\frac{1}{M_0} = \frac{1}{M} + \langle n_i \rangle_{ad} \left[\frac{1}{M+m} - \frac{1}{M} \right] = \frac{1}{M} \left[1 - \langle n_i \rangle_{ad} \frac{m}{M+m} \right] \quad (3)$$

$$\nu_0 = \nu + \frac{1}{2} \langle P^2 \rangle_{ph} \left[\frac{1}{M+m} - \frac{1}{M} \right]$$

$$\kappa = \langle J(\mathbf{R}_i - \mathbf{R}_j) \rangle_{ph}$$

where $\langle \dots \rangle_{ph}, \langle \dots \rangle_{ad}$ denotes the thermal average with the Hamiltonians H_{ph} and H_{ad} . This means that now the lattice parameters ($M_0, A_{ik}^{\alpha\beta}$) and the adatom parameters (ν_0, κ) depend on the temperature T .

III. THE FREQUENCY SPECTRUM OF A SURFACE WITH ADSORBED ATOMS

In accordance with the Bogolyubov variational method we shall investigate two additive systems. Their coupling is included in the parameters $\kappa, A_{ik}^{\alpha\beta}, M_0$ and ν_0 defined by (3). In order to analyse the behaviour of the frequency spectrum, we have to specify the structure and the interactions between the surface atoms and between adatoms, i.e. the potentials $\Phi(\mathbf{R}_i - \mathbf{R}_j)$ and $J(\mathbf{R}_i - \mathbf{R}_j)$. We shall assume the simplest case when the surface has a structure of the simple square lattice with interactions (central and non-central) between nearest neighbours only. The

adatoms interact with their nearest neighbours by central forces only. We assume further that the interaction surface — system of adatoms leads, besides changes in the interaction constants and the masses of the surface atoms, to a change of the lattice parameters, but without changing the shape of the cell.

For this reason **A** in equations (2, 3) is the force constant matrix of the simple square lattice. It is diagonal with two nonzero elements (A_1 — the central, A_2 — the non-central). The frequencies of the surface vibrations are then given by the known relation [9]

$$\omega_{j=1}^2(q) = \frac{2}{M_0} [A_1(1 - \cos q_1 a) + A_2(1 - \cos q_2 a)] \quad (4)$$

and cyclic for the polarization $j=2$, where a is the lattice parameter, q is the wave vector with components q_1 and q_2 . The displacement correlation function is given by the formula

$$\langle (X_{ij}^a)^2 \rangle_{\mu\kappa} = \frac{\hbar}{2NM_0} \sum_{q_j} \frac{1 - \cos q_j a}{\omega_j(q)} \coth \frac{1}{2} \beta \hbar \omega_j(q) \quad \beta = (kT)^{-1}.$$

The correlation function may be found analytically only in the high temperature limit

$$\langle (X_{ij}^a)^2 \rangle_{\mu\kappa} = \frac{1}{\pi\beta A_1} \left[\arctg \sqrt{\frac{A_1}{A_2}} + \frac{A_1}{A_2} \operatorname{arccoth} \sqrt{\frac{A_1}{A_2}} \right]. \quad (5)$$

It is convenient to define the potentials $\Phi(\mathbf{R}_i - \mathbf{R}_j)$ and $J(\mathbf{R}_i - \mathbf{R}_j)$ by means of the coefficients of their expansions. Then, as it was shown in [8], for our model of the surface and adatom system the first and third equation of (3) has the simple form

$$\begin{aligned} A_1 &= B_1 + c \langle n_i n_j \rangle_{ad} \\ A_2 &= B_2 \end{aligned} \quad (6)$$

$$\kappa = \langle J(\mathbf{R}_i - \mathbf{R}_j) \rangle_{\mu\kappa} = J_0 - b \bar{X}_0 + \frac{c}{2} [(\bar{X}_0)^2 + \langle (X_{ij}^a)^2 \rangle_{\mu\kappa}] \quad (7)$$

where B_1 and B_2 are the non-zero elements of the force constant matrix of the clean surface, or in other words, B_1 and B_2 are the second-order terms in the expansion of $\Phi(\mathbf{R}_i - \mathbf{R}_j)$ about the equilibrium positions of the clean surface atoms (the first-order terms are identically zero). b and c are the first and the second-order terms in the similar expansion for $J(\mathbf{R}_i - \mathbf{R}_j)$. The quantity \bar{X}_0 expresses the change of the atomic equilibrium positions if gas atoms are adsorbed on the surface. As the atomic equilibrium positions $\langle \mathbf{R}_i \rangle$ are determined by the

boundary conditions represented by the external isotropic pressure p acting in the surface plane, from the force equilibrium condition for the surface atoms the following relation can be derived

$$\bar{X}_0 = \frac{-\frac{pD}{a} + b \langle n_i n_j \rangle_{ad}}{B_1 + c \langle n_i n_j \rangle_{ad}}.$$

If we now express $\langle n_i \rangle_{ad}$ and $\langle n_i n_j \rangle_{ad}$ as the functions of v_0 and κ , then the close system of equations (3), (5), (6), (7) may be solved and the surface atom frequencies (4) evaluated.

For $\langle n_i \rangle_{ad}$ and $\langle n_i n_j \rangle_{ad}$ the following approximations were used:

1) Molecular field approximation (MFA 1)

$$\langle n_i n_j \rangle_{ad} = \langle n_i \rangle_{ad}^2 \quad (8)$$

$$\langle n_i \rangle_{ad} = [1 + \exp \beta (v_0 + 4\kappa \langle n_i \rangle_{ad})]^{-1}$$

for arbitrary neighbouring lattice sites i and j .

2) Molecular field approximation (MFA 2)

$$\langle n_i n_j \rangle_{ad} = \langle n_i \rangle_{ad} \langle n_j \rangle_{ad} \quad (9)$$

if the lattice is divided into two interpenetrating lattices described by $\langle n_i \rangle_{ad}$ and $\langle n_j \rangle_{ad}$ (a chessboard structure).

3) Quasichemical approximation

$$\langle n n \rangle_{ad} = \langle n \rangle_{ad} \frac{r-1+2\langle n \rangle_{ad}}{r+1} \quad (10)$$

$$\langle n \rangle_{ad} = \left[e^{-\beta(v_0+2\kappa)} \left(\frac{r+1-2\langle n \rangle_{ad}}{r-1+2\langle n \rangle_{ad}} \right)^2 + 1 \right]^{-1}$$

$$r^2 = 1 - 4\langle n \rangle_{ad}(1 - \langle n \rangle_{ad})(1 - e^{-\beta\kappa})$$

where for $\kappa \geq 0$ there is $r \leq 1$.

4) Polynomial decoupling

$$\langle n n \rangle_{ad} = \sum_{k=0}^4 \frac{k}{4} C_k^2 \langle n \rangle_{ad}^k (1 - \langle n \rangle_{ad})^{4-k} N_k \quad (11)$$

$$\langle n \rangle_{ad} = \sum_{k=0}^4 C_k^1 \langle n \rangle_{ad}^k (1 - \langle n \rangle_{ad})^{4-k} N_k$$

$$N_k = [1 + \exp \beta (v_0 + k\kappa)]^{-1}.$$

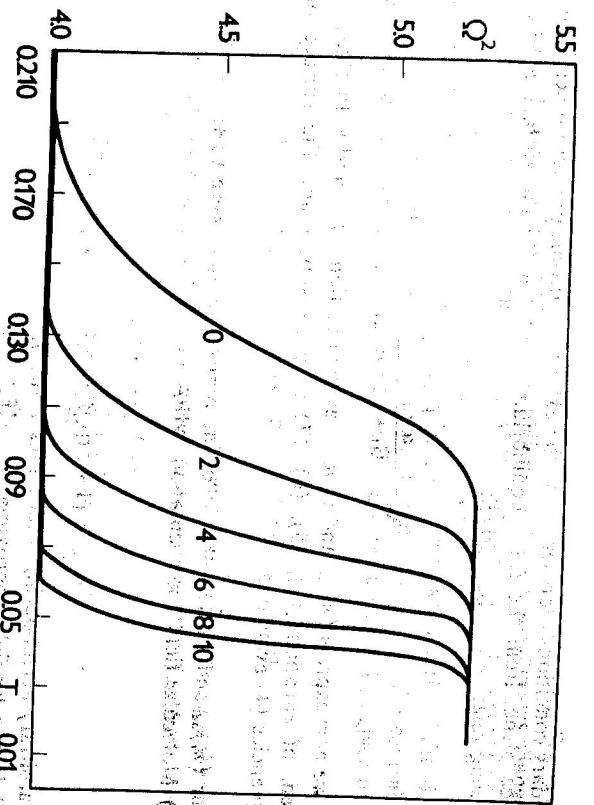


Fig. 1. The dimensionless surface atom frequency Ω^2 , corresponding to the wave vector $q = (\frac{\pi}{a}, 0)$, in the quasichemical approximation (10) as a function of temperature T and gas pressure $P = P_0 e^{-\epsilon T}$, in numbers at the curves mean the value of ϵX . The mass ratio of the surface atom to the gas atom is $M/m = 57.81$.

IV. RESULTS AND DISCUSSION

All our numerical calculations of the surface frequencies have been performed with dimensionless quantities. The choice of the constant approximately corresponds to the chemisorption on the real crystal surface, where the resulting nearest-neighbour interactions are, with few exceptions, mainly repulsive ($J_0 > 0$). We have put $J_0 = 0.15$, $\epsilon = 2$, $ba = 0.11$, $c/B_2 = 1$, $B_1 a^2 = 8$, $B_1/B_2 = 3$, $vp = 0.03$. The mass ratio is either $M/m = 57.81$ or $M/m = 6$. The ratio of the masses $M/m = 57.81$ corresponds to hydrogen on the crystal surface of N_2 . The lattice dynamic quantities $\langle P_i^2 \rangle_{st}$ and $\langle X_k \rangle_{st}^2$ have been evaluated in the high temperature limit. The dimensionless surface atom frequency $\Omega^2 = M\omega^2/B_1$, corresponding to the wave vector $q = (\pi/a, 0)$, has been calculated in the approximations (8)–(11). Typical results are shown in Fig. 1–3, where Ω^2 is plotted as a function of T . Here the effect of gas pressure is illustrated, too. It is evident that at high temperature the crystal surface is clean and the surface atoms vibrate with the frequencies which do not depend on temperature.

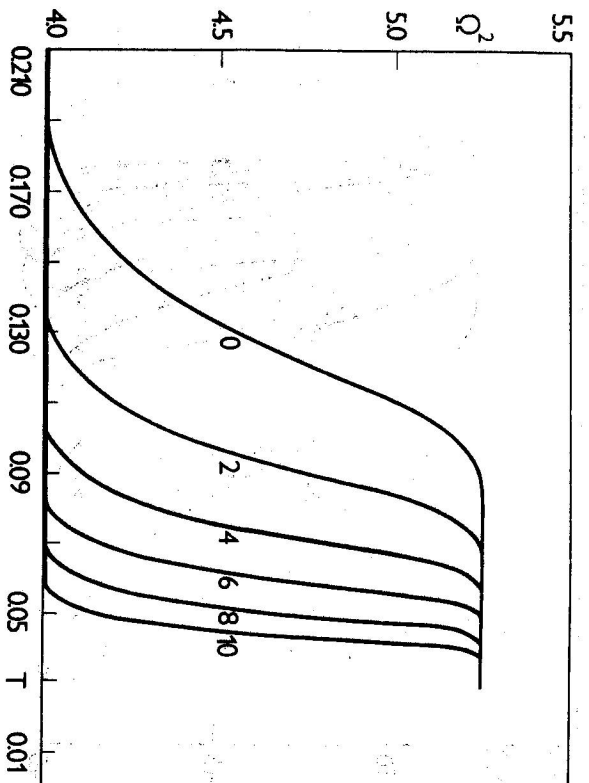


Fig. 2. The same as Fig. 1, but in the polynomial decoupling (11).

In our case the surface frequency Ω^2 is equal to 4. With decreasing temperature, at constant gas pressure, gas atoms are adsorbed on the crystal surface and Ω^2 becomes a function of temperature T . The maximum value of Ω^2 depends on the adatom mass and corresponds to the coverage $\Theta \equiv \langle n \rangle = 1$ when the monolayer of the gas atoms is adsorbed. It follows from (4) that the growing force constant raises the surface frequencies while the effect of the growing mass of atoms is opposite. In all the approximations except MFA 2 (see below Figs. 7–8, where the functions Θ and $\langle nn \rangle_{st}$ are displayed), M_0 and A_1 are monotone increasing in magnitude if T decreases. For the mass ratio $M/m = 58.71$, that is for the light gas atom mass, the change of the mass of surface atoms has a small influence on the frequency curves and these are non-decreasing in the temperature region where $\langle nn \rangle_{st}$ are small. Only in the approximation MFA 2, in which the correlations between neighbouring adatoms are overestimated (the dashed lines in Fig. 3), the effect of the mass can exceed the effect of the force constant and the surface frequency can decrease with decreasing temperature.

There is a different situation in case of the heavy gas atoms, in our case we have $M/m = 6$. Here the influence of the changing mass is also seen at the small coverage, as illustrated in Figs. 4–6. All the curves start at $\Omega^2 = 4$ and then they decrease due to the increasing mass of surface atoms. The decrease of frequencies

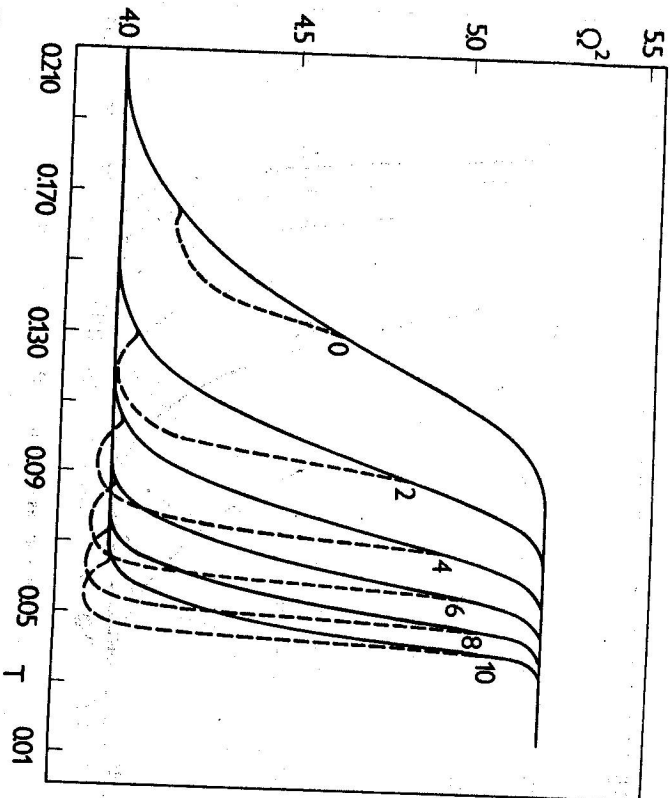


Fig. 3. The same as Fig. 1, but in molecular field approximations. The solid lines correspond to MFA 1 (8), the dashed lines correspond to MFA 2 (9) — to the upper branch (see Fig. 8). For a given P MFA 2 differs from MFA 1 only in the middle part of the curves.

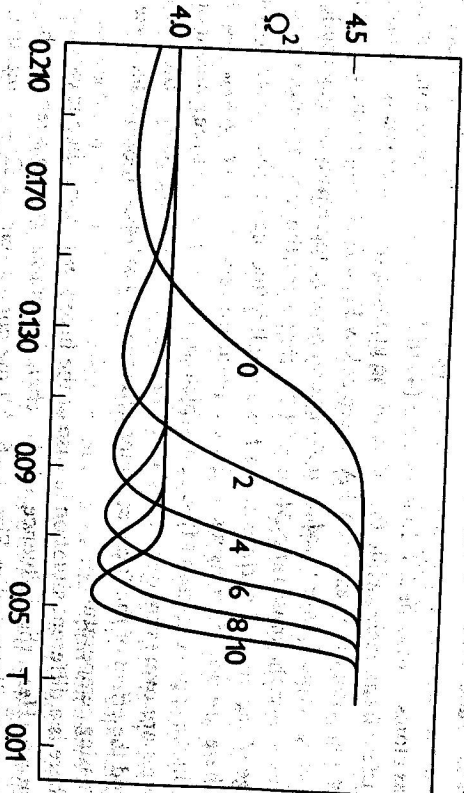


Fig. 4. The same as Fig. 1, but for the mass ratio $M/m = 6$.

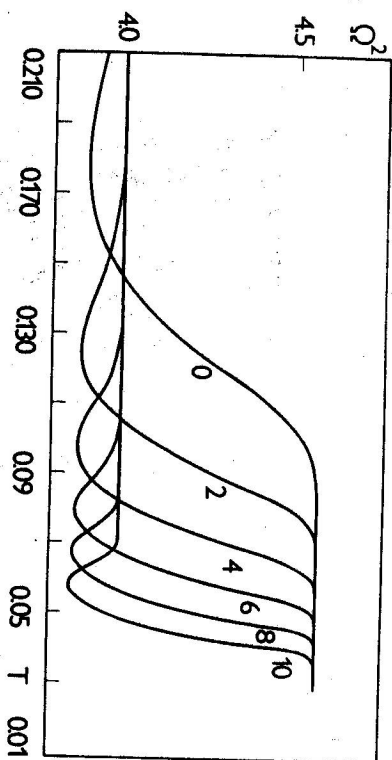


Fig. 5. The same as Fig. 2, but for the mass ratio $M/m = 6$.

depends on the correlations between the adatoms. If these are neglected, i.e. if $\langle mn \rangle = \langle n \rangle^2$ (MFA 1), the frequency reaches the minimum at the coverage $\Theta = 0.225$ as it follows from (4). This minimum frequency is the same for all P (see Fig. 6).

Fig. 7 shows the typical behaviour of $\langle n \rangle$ and $\langle mn \rangle$ in the quasichemical

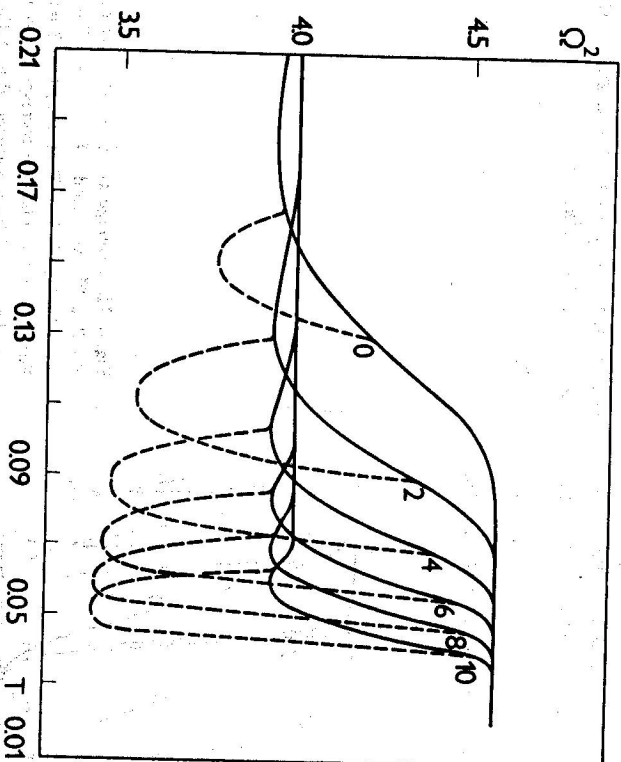


Fig. 6. The same as Fig. 3, but for the mass ratio $M/m = 6$.

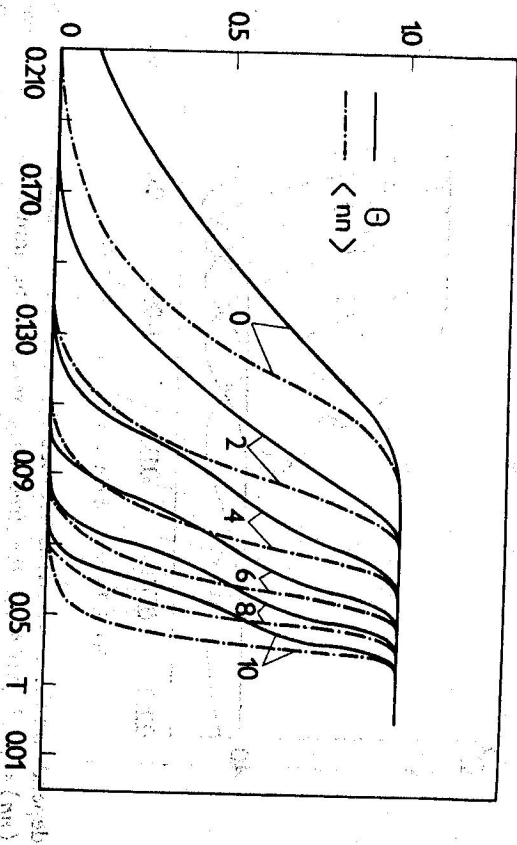


Fig. 7. The coverage (the solid lines) and the correlation function (the dot-and-dashed lines) as functions of temperature T and gas pressure $P = P_0 e^{-T}$ for the mass ratio $M/m = 57.81$. The calculations are performed in the quasichemical approximation (10).

approximation. The behaviour of these functions in the polynomial approximation is practically the same. For these approximations the relation

$$\langle mn \rangle \cong \langle n \rangle^2 e^{-\kappa}, \quad \kappa > 0$$

is satisfied if the coverage is small.

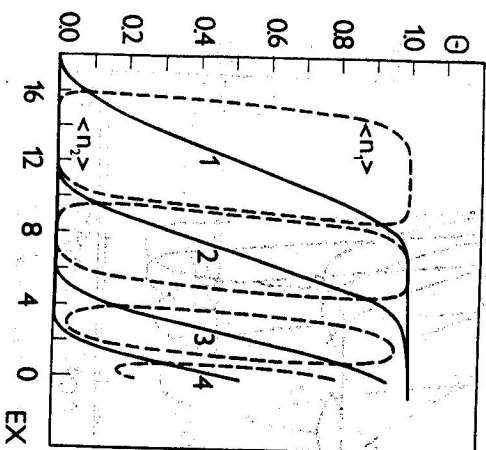


Fig. 8. The coverage as a function of gas pressure $P = P_0 e^{-EX}$ at fixed T (1 — $T = 0.045$, 2 — $T = 0.065$, 3 — $T = 0.105$, 4 — $T = 0.150$). For each T the solid line corresponds to MFA 1 (8), the dashed lines correspond to MFA 2 (9). The mass ratio is $M/m = 57.81$.

The adsorption isotherms evaluated in the molecular field approximation are shown in Fig. 8. The dependence of Θ versus T at fixed gas pressure has a similar character. It is known that our model of an adsorbing surface does not exhibit first-order phase transitions if the nearest neighbour interaction is repulsive ($\kappa > 0$). Our results agree with this prediction.

REFERENCES

- [1] Somorjai, G. A., Van Hove, M. A.: *Adsorbed Monolayer on Solid Surfaces*. Springer Verlag, Berlin 1979.
- [2] Roelofs, L. D., Estrup, P. J.: *Surface Sci.*, 125 (1983), 51.
- [3] Sinha, S. K. Ed.: *Ordering in Two Dimensions*. North Holland, New York 1980.
- [4] Schick, M.: in *Real Space Renormalization*. Eds.: T. W. Burkhardt, J. M. J. van Leeuwen. Springer, Berlin 1982.
- [5] Šurda, A., Karasová, I.: *Czech. J. Phys. B* 33 (1983), 287.
- [6] Barker, R. A., Estrup, P. J.: *Phys. Rev. Lett.* 41 (1978), 3107.
- [7] Ertl, G., Norton, P. R., Rüstig, J.: *Phys. Rev. Lett.* 49 (1982), 177.
- [8] Karasová, I., Fedyanin, V. K., Šurda, A.: *Acta phys. slov.* 31 (1981), 39.
- [9] Maradudin, A. A., Montroll, E. W., Weiss, G. H.: *Theory of Lattice Dynamics in the Harmonic Approximation*. Mir, Moscow 1965.

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