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On the ordering phenomena in adsorbed layers

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This article gives a brief survey of phase transitions in adsorbed films on well defined surfaces of different symmetry of the lattice. The discussion concentrates on the effects of periodic changes of the adsorbate – substrate potential on the structure and thermodynamic properties of adsorbed films. Different theoretical approaches are briefly reviewed, with an emphasis on those which explicitly take into account finite corrugation of the surface potential.

1. INTRODUCTION

The formation of ordered structures in adsorbed films formed on well defined crystal surfaces has been attracting a great deal of interest for many years [1-5] and the activity in this field is still growing. At present, the literature which presents the results of both experimental and theoretical studies is overwhelmingly abundant and the achievements are outstanding. The progress in this field has gained a particular impetus due to introduction of powerful experimental techniques (e.g., neutron scattering [6,7], various forms of electron spectroscopy [8-14], light particle, e.g. helium, scattering [15,16], and many others [17-21]), the extensive use of computer simulation methods (Monte Carlo and molecular dynamics) [5,22-28] and, last but surely not least, owing to very intensive theoretical studies [1-3,29-36].

The systematic investigation of phase transitions in adsorbed layers began in the late sixties [1,37-39] just after the development of the technology for the production of the graphite substrate with highly uniform surface [40]. Thomy and Duval [37-39] measured adsorption isotherms of simple gases (krypton, xenon, methane) on graphite at low temperatures and demonstrated that monolayer films exhibit the two-dimensional counterparts of gas, liquid and solid phases. Over the next years, hundreds of papers reporting the new findings were published and particularly extensive studies were carried out for the films formed on graphite [41-44]. It soon became clear that several phenomena observed in adsorbed films do not have simple counterparts in the threedimensional bulk matter. The misfit between the lattice spacing of the substrate surface and the preferred lattice spacing of the adsorbate (determined by the interactions between the adsorbed particles) leads to the formation of incommensurate phases, axially ordered phases and other forms of ordering specific to surface systems. All those findings clearly demonstrated that spatial nonuniformities of the gas – solid potential, resulting directly from the lattice structure of the crystal surface, are of great importance and often determine the structure of adsorbed layers.

In the case of hexagonal lattices (e.g. graphite surface), the intrinsic lattice constant of the adsorbed film, however usually is different from the distance between the adjacent minima of the potential wells at different surface cells, but nevertheless, the symmetry of the substrate potential and the symmetry of the adsorbate preferential structure are the same. Thus, for small misfit, even a slight corrugation of the substrate potential may considerably stabilize the commensurate phase [1,43], while for large misfit, incommensurate phases are formed [45,46].

In the cases of square and rectangular lattices, the surface corrugation potentials exhibit usually much higher periodic variations [1] and there is a natural difference in the symmetries of such lattices and the preferred symmetry of the adlayers. Thus, the competition between the adsorbate – adsorbate and the adsorbate – adsorbent interactions must be much stronger and may lead to the formation of the new types of ordering in the film. Indeed, several experimental studies have revealed the existence of the higher order commensurate phases [47,48] and axially ordered phases [12,14,49,50], in addition to the registered and incommensurate (floating solid) phases. The mechanisms of phase transitions between all those different types of surface phases are quite complex and are not so well described and understood as in the case of hexagonal surfaces.

In this paper, we tackle several questions concerning general aspects of the formation and properties of the adsorbed films deposited on crystal surfaces of different symmetry and our discussion is primarily directed towards the presentation of recent studies performed for such systems with help of computer simulation methods.

2. THE GAS - SOLID INTERACTION

Here, we assume that the surface exposed to the gas phase is a perfect single plane of a crystal. In such a simple situation we can fully characterize the surface lattice by its unit lattice vectors \vec{a}_1 and \vec{a}_2 (Figure 1). The interaction of the gas atom with the crystal can be represented by the potential $v = (\vec{\tau}, z)$, where $\vec{\tau} = (x, y)$ is the two-dimensional vector specifying the location of the

adatom in the plane parallel to the surface and z is the distance from the surface, located at z=0 and assumed to run through the centers of the uppermost layer of the crystal atoms. The periodic structure of the crystal surface causes that the potential $v(\vec{\tau}, z)$ is also a periodic function, such that

$$v(\vec{\tau}, z) = v(\vec{\tau} + k_1 \vec{a}_1 + k_2 \vec{a}_2, z)$$
(1)

where k_1 and k_2 are integers. This periodicity property of the potential $v(\vec{\tau}, z)$ has prompted Steele [51] to represent $v(\vec{\tau}, z)$ in the form of the Fourier series

$$\nu(\vec{\tau}, z) = \nu_0(z) + \sum_{\vec{q}\neq 0} \nu_{\vec{q}}(z) \exp\left[i\vec{q}\cdot\vec{\tau}\right]$$
(2)

where $v_0(z)$ is the interaction potential averaged over the entire surface and the sum runs over the nonzero two-dimensional reciprocal lattice vectors \vec{q}

$$\vec{q} = n_1 b_1 + n_2 b_2 \tag{3}$$

where \vec{b}_1 and \vec{b}_2 are the basic reciprocal lattice vectors and n_1 and n_2 are integers.



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Figure 1. (a) Top view of the fcc(100), (110) and (111) surfaces showing the surface unit cell vectors \vec{a}_1 and \vec{a}_2 . The lengths of the unit cell vectors for (110) and (111) surfaces are expressed in units of \vec{a}_1 for the (100) surface. (b) Examples of different ordered superstructures on a square lattice. The adsorbate layer unit lattice cell vectors are shown for the structure 9

The usefulness of the expansion (2) depends primarily on how fast it converges. It turns out that the convergence of the series is quite fast for the graphite basal plane and for (100) and (111) faces of the fcc crystal [51,52]. On the other hand, for the (110) plane of the fcc crystal it is necessary to include significantly more terms in order to obtain reliable results [53].

The expressions for the Fourier coefficients derived by Steele have rather limited application to real systems, since the Lennard-Jones potential is not the best choice for the representation of two body interactions in adsorption on ionic crystals, e.g., NaCl and MgO, or on metals.

Recent experimental [54] and theoretical [55,56] studies have demonstrated that even the closed packed faces of metal crystals, e.g. Pt(111), show quite strong periodicity of the surface potential, against a wide-spread belief [57,58] that such surfaces can be considered as essentially noncorrugated.

In fact, there are not so many direct and reliable estimations of the surface corrugation potential, apart from rather well known examples of simple gases on graphite [59], lamellar dihalides [60], and on some close packed metal surfaces [16]. It should be noted that even in the case of simple gases adsorbed on graphite, for which the interaction potentials are believed to be known quite well, it turns out that the corrugation effects are probably higher than obtained from theoretical calculations. It has been demonstrated by computer simulations [61-66] that in order to obtain a good agreement with experimental data the periodic variations of the surface potential need to be higher. To take this effect into account, the expression (2) has been modified [61] by introducing the adjustable "corrugation parameter" V_b , so that eqn. (2) takes the following form:

$$v(\vec{\tau}, z) = v_0(z) + V_b \sum_{\vec{q} \neq 0} v_{\vec{q}}(z) \exp\left[i\vec{q} \cdot \vec{\tau}\right]$$
(4)

For the values of $V_b > 1$, the effects due to the corrugation are enhanced with respect to those predicted by eqn. (2), while for $V_b < 1$ they are weakened.

In many cases, to study basic effects of the surface potential corrugation and the surface lattice symmetry it suffices to retain only very few leading terms in the expansion (2) (or (4)) and consider the Fourier amplitudes as adjustable parameters. A good example of such approach is the study performed by Bruch and Venables [67], who considered the conditions that must be satisfied by the system geometry and the binding potential in order to stabilise uniaxially ordered structures in monolayer films. The above assumption is justified by the known property of the Fourier coefficients $v_{\bar{q}}(z)$, which usually decay rapidly with $|\bar{q}|$ and z. In many cases this decay is exponential [51], i.e.,

$$v_{\vec{q}}(z) \propto \exp\left[-\left|\vec{q}\right|z\right]$$
(5)

From the above property of the corrugation potential, we immediately conclude that its direct effect on the admolecules located beyond the first layer is bound to be very weak, if any at all. It does not mean, of course, that the structure of the second and higher layers is unaffected by the properties of the surface potential. The attraction between admolecules and the surface is responsible for the formation of subsequent adsorbed layers and its strength is a chief factor determining the film growth mode [34], as well as internal structure of particular layers. The effects due to the surface corrugation are transmitted to the higher layers through the interaction with the admolecules from the first layer, which are under a strong influence of the surface corrugation potential. These effects have been demonstrated by the molecular dynamics simulation of Phillips and Shrimpton [66], as well as by the Monte Carlo study of Patrykiejew et al. [68,69].

The properties and structure of adsorbed films are controlled by the combined effects due to admolecule – admolecule and admolecule – substrate interactions as well as by the imposed thermodynamic constraints (specified temperature, film density, bulk gas pressure). Of course, in real situations, as well as in computer simulations, the effects due to finite size of the surface may considerably affect the structure of adlayers [68], but we shall not discuss such problems here.

In general, at low temperatures the adsorbate – adsorbate interaction tends to enforce the formation of hexagonal close-packed (hcp) solid phase in monolayer films, while the corrugated admolecule – substrate potential favours the formation of registered structures. A simple criterion enabling to classify the adsorbed films with respect to their structure has been developed by Park and Madden [70]. Assuming that the substrate surface lattice unit cell vectors are \vec{a}_1 and \vec{a}_2 and the overlayer unit cell is characterized by the unit vectors \vec{e}_1 and \vec{e}_2 the relation between these two sets can be written as

$$\begin{bmatrix} \vec{e}_1 \\ \vec{e}_2 \end{bmatrix} = \begin{bmatrix} \alpha_{11} & \alpha_{12} \\ \alpha_{21} & \alpha_{22} \end{bmatrix} \begin{bmatrix} \vec{a}_1 \\ \vec{a}_2 \end{bmatrix}$$
(6)

Park and Madden have classified the adsorbed layers with respect to the behavior of $det[\alpha_{ij}]$ and singled out three cases. The first case groups all systems for which $det[\alpha_{ij}]$ is an integer number. This situation corresponds to the registered or commensurate adsorbed films. The second case involves the situations in which $det[\alpha_{ij}]$ is a rational number. When this condition is satisfied the adsorbed film forms the so-called "high-order" commensurate phase, with only a certain fraction of adatoms located directly over the adsorbed layer is incom-

mensurate with the substrate surface lattice. The above classification parametrises the adsorbed layer structure with respect to the relative sizes of the surface and adlayer unit cells. The area of the surface unit lattice cell is given by $\vec{a}_1 \times \vec{a}_2$, and the area of the adsorbed layer unit cell is equal to $\vec{e}_1 \times \vec{e}_2$, so that det α_{ii} is equal to the ratio of these two areas.

The criterion of Park and Madden vastly oversimplifies the reality. The distinction between the incommensurate and the high-order commensurate phases may cause problems, as it is usually possible to approximate irrational number by a suitably chosen rational number that falls into the region of experimental resolution. Aubry [71] has even proposed to consider any incommensurate adsorbed layer as sufficiently high-order commensurate phase. When the conditions change and the density of the film increases or decreases, it is supposed that the resulting changes in the film structure are due to a series of first-order transitions between different high-order commensurate phases. This leads to the so-called "devil's staircase" of phase transitions.

Another weakness of the above criterion is that it does not include incommensurate phases exhibiting domain walls networks [45,72]. In such cases the incommensurate phase is composed of large commensurate domains separated by walls which can have different structure, thickness and orientation.

A useful measure of the relative size of the adsorbate and the surface lattice unit cell is the so called dimensional incompatibility parameter [60], defined as

$$I = (a - r_1) / r_1 \tag{7}$$

where *a* is the surface lattice constant and r_1 is the distance between adjacent adsorbate atoms in the surface phase. Of course, in the case of a rectangular symmetry of the surface lattice, one can define two different dimensional incompatibility parameters I_1 and I_2 , by taking $a = |\vec{a}_1|$ and $a = |\vec{a}_2|$. The behavior of films formed on corrugated surfaces is closely related to the magnitude of the parameter I [60,73].

3. LATTICE GAS MODELS

The interaction between the particles adsorbed on a lattice can be represented by the potential u(r), where r assumes discrete values:

$$r = \sqrt{k^2 a_1^2 + l^2 a_2^2} \tag{8}$$

In the above a_1 and a_2 are the lengths of the unit cell vectors and k and l are integers. The possible ordered structures that can appear in the system are primarily determined by the lattice symmetry and the properties of the potential u(r). Usually, u(r) is a sum of contributions arising from repulsive and attrac-

tive interactions. For example, assuming that u(r) is given by the Lennard-Jones potential, the effect of repulsive forces can be related to the relative size of adatoms, measured by the parameter σ and the size of the surface unit cell, measured by the lattice constants a_1 and a_2 . It is convenient to introduce the reduced quantities and express all the distances in units of, say, a_1 . Note that in the case of a square lattice, eg. (100) plane of the fcc crystal, $a_2 = a_1$, while for the (110) plane of the fcc crystal $a_2 = \sqrt{2}a_1$. Also, the energy-like quantities, as well as the temperature, can be expressed in units of ε .

Lattice gas model provides a simple explanation for the experimentally observed changes in the critical temperature of adsorbed monolayers resulting from the changes of the dimensional incompatibility between adsorbate and adsorbent (cf. eqn. (7)). Note that in the case of a lattice gas model, a simple mean field approximation gives

$$T_c^{MF} = \frac{U_{sum}}{2k} \tag{9}$$

where

$$U_{sum} = -0.5 \sum_{j} u(r_j) \tag{10}$$

where the sum runs over different shells of neighbors. In the particular case of Lennard-Jones interaction potential, truncated at $2.5\sigma^*$, U_{sum} is given by [73]

$$U_{sum} = -8\varepsilon \left[C_{12} \sigma^{*12} - C_6 \sigma^{*6} \right]$$
(11)

where $C_{12} = 1.015997141$ and $C_6 = 1.156625$. Thus, the critical temperature is proportional to U_{sum} , which varies with σ^* . Of course, the same is true for more rigorous treatments, as it is illustrated by the results shown in Figure 2a and 2b. The only available experimental data that clearly demonstrate changes of the two-dimensional critical temperature with dimensional incompatibility correspond to adsorption on a honeycomb lattice of lamellar dihalides [60] (cf. Figure 2c). Nevertheless, the qualitative picture should be the same in the case of adsorption on a square lattice. Of course, the predictions stemming from lattice gas models do not directly apply to adsorption on rather weakly corrugated surfaces of lamellar dihalides and are, at the most, only qualitatively correct.



Figure 2. Two-dimensional critical temperature versus U_{sum} for the Lennard-Jones particles of different diameter, $\sigma^* = \sigma/a$, (shown in the figure) on a square lattice, obtained from mean field approximation (part a) and from the coherent anomaly theory (part b). Part c shows the ratio of two-dimensional and three-dimensional (bulk) critical temperatures for simple gases adsorbed on lamellar dihalides (from Ref. 73)

Lattice gas models work much better for strongly adsorbed (chemisorbed) species. Good examples of such a system are the monolayers of atomic hydrogen adsorbed on Pd(100) [11] and on W(100) [74], Cl adsorbed on Ag(100) [75] and O atoms adsorbed on Cu(100) [76]. It is particularly interesting that even very simple lattice models allow to obtain rather good agreement with experimental data. For instance, hydrogen adsorbed on W(100) orders into $c(2\times 2)$ phase at low temperatures. The simplest possible model which predicts

that form of ordering is the Ising-like model with nearest-neighbor repulsive interactions only. Monte Carlo simulation for such a model [77] led to rather good agreement between the calculated and measured temperature changes of the intensity of a LEED spot for the $c(2\times 2)$ phase.



Figure 3. Coverage dependence of the (1/2, 1/2) LEED beem height at 300K for the atomic Cl adsorbed on Ag(100) surface (part a), and the structure factor obtained from Monte Carlo simulation on the 72×72 lattice (part b). (Adapted from Ref. 75)

A quite similar model was also found suitable to describe the dissociative adsorption of chlorine on Ag(100) surface. A monolayer film of atomic Cl on Ag(100) was found to form the $c(2\times2)$ phase [77,78]. Taylor et al. [75] performed Monte Carlo simulations for a model with infinite nearest-neighbor repulsion on a 72×72 lattice and found a good agreement with experimental data. In particular, the calculated structure factor versus coverage reproduces quite well the measured LEED beem height (see Figure 3). A rather convincing

proof of adequacy of the Ising model representation for that system is the "Fisher renormalized" exponent $\beta / (1-\alpha) \approx 0.12$ evaluated from experimental data and which agrees very well with the exact Ising value of 0.125.

Although the formation of $c(2\times2)$ ordered phase is quite common in atomic monolayers on metals, there are also known numerous examples of systems which also show other ordered phases. For example, atomic oxygen adsorbed on Rh(100) was found to form the $p(2\times2)$ structure of the density 0.25 [79], which then undergoes transition to a denser $c(2\times2)$ structure. The same was found for O/Pd(100) [67] and Se/Ni(100) [80]. The phase diagram for the last system was evaluated by reflection high-energy electron diffraction (RHEED) [80] and was also studied by Monte Carlo simulation [80,81]. Analysis of experimental data, model calculations and symmetry arguments led to the conclusion that Se/Ni(100) phase diagram is topologically equivalent to the Ashkin-Teller model [82]. In this model, each lattice site is characterized by two Ising spins, s_i and t_i , and the Hamiltonian reads:

$$\mathbf{H} = -J \sum_{\langle i,j \rangle} (s_i s_j + t_i t_j) - \Lambda \sum_{\langle i,j \rangle} s_i t_i s_j t_j$$
(12)

Critical properties of that model are believed to be non-universal and dependent on the ratio Λ/J . Monte Carlo study was performed [80] for a simple lattice gas model with interactions up to fourth nearest neighbor which yields the phase diagram belonging to the universality class of Ashkin-Teller model. Figure 4 shows that the experimental Se/Ni(100) phase diagram and the phase diagram obtained for the above lattice gas (Ashkin-Teller-like) model are quite similar, indeed.

Extension of the lattice gas formalism from two- to three-dimensional adsorption system is straightforward [34,83]. Assuming that the adsorbate – substrate interaction is represented by the potential v(z), where z is the distance from the surface, the Hamiltonian for such a model reads

$$H = \sum_{i} v(z_{i})n_{i} + \frac{1}{2} \sum_{i \neq j} u(r_{ij})n_{i}n_{j}$$
(13)

Note that in the lattice gas language, z_i can take upon only discrete values determined by the distance of the *i*-th site from the surface, given by the number of layer *l*. Depending on the properties of the potentials v(z) and u(r) the system shows different behavior [34,84-89].



Figure 4. A comparison of experimental and theoretical phase diagrams for selenium on Ni(100) surface. (From Ref. 80)

Systematic analysis of lattice gas model representation of multilayer adsorption was done by Pandit et al. [34] for the potential v(z) given by

$$v(l) = V_0 \delta_{11} + Bl^{-3} \tag{14}$$

where V_0 is the energy of adsorption for the first adsorbed layer. They presented a very elegant and detailed discussion of possible scenarios for the film growth on the basis of mean field theory for lattice gas model. More recently this problem was also considered by Prasad and Weichman [90], who used both the mean field theory and the renormalization group arguments.

Here we briefly discuss the main predictions stemming from the lattice gas model assuming that $B = V_0$ in eqn. (14) and neglecting all but the first nearest neighbor interactions between adsorbate atoms.



Figure 5. An example of experimental adsorption isotherm for Argon on MgO at T = 60.8 K (adapted from Ref. 91) (part a) and isotherms obtained from Monte Carlo study (part b) for a cubic lattice gas model (from Ref. 88)

When the ratio V_0/u ($u = u(r_{NN})$) is sufficiently high, *i.e.*, when the surface is highly attractive towards the adsorbate, the film grows in a layer-by-layer mode (see Figure 5) which was observed in many real adsorption systems [3,41,60,91]. At low temperatures it corresponds to the presence of the series of layering transitions which terminate at the corresponding critical points $T_c(l)$. From the mean-field theory it follows that

$$\lim T_c(l) = T_c^{3D} \tag{15}$$

where T_c^{3D} is the critical temperature of the uniform bulk gas, while the exact result is [34]

$$\lim_{c} T_c(l) = T_R \tag{16}$$

where T_R is the roughening temperature, which in general is much lower than T_c^{3D} and only slightly exceeds $T_c(1)$ and the following relation is predicted [92] to be obeyed

$$T_R - T_c(l) \propto (\ln l)^{-2}, \qquad l \to \infty$$
 (17)

In the above situation the adsorbate wets the surface at any temperature down to T = 0.

As the adsorbate – substrate interaction becomes weaker and the following condition is met

$$\frac{V_0}{u} < \left[\sum_{l=1}^{\infty} l^{-3}\right]^{-1} \tag{18}$$

the adsorbate does not wet the surface at T = 0, but may still exhibit complete wetting at the temperatures which exceed the wetting temperature T_w . Thus, below T_w the film thickness remains finite up to the bulk condensation point, while for $T > T_w$ we observe again the formation of macroscopically thick adsorbed film as the chemical potential approaches its bulk coexistence value. That change of the film behavior at T_w marks the so-called wetting transition which can be either the first-order or the continuous transition (critical wetting) depending on the value of V_0/u and on the range of molecular interactions in the system [93]. When the wetting transition is first-order it is often preceded by the *prewetting transition* between the thin and thick film. The prewetting transition occurs at the chemical potential below the bulk coexistence value. As the temperature increases the prewetting transition terminates at the corresponding critical point. Due to the finite extent of thin and thick films, on the both sides of the prewetting transition, it belongs to the universality class of the twodimensional Ising model. This situation corresponds to the so-called intermediate substrate regime. One can interpret the wetting transition at T_w as an interface unbinding transition [94]. At temperatures below T_w , in the non-wet region, the gas-liquid interface is very tightly bound to the substrate surface and only a small density enhancement near the wall occurs. In the wet state this density enhancement is large and even exceeds the density of the bulk liquid over quite large distances from the surface and the interface between the liquid layer and the bulk gas phase is a smooth, delocalized object of large height amplitudes $z_i(x, y)$. The wetting transition temperature grows as the ratio V_0/u becomes lower. When it reaches a certain limiting value, the wetting temperature reaches the bulk critical point of the adsorbate, and for still lower V_0/u one enters the so-called weak substrate regime. In this case the adsorbate does not wet the substrate under any conditions and adsorption is always finite.



Figure 6. (a) Phase diagram in the coverage (θ) – temperature $(T^* = kT/J)$ where J is the exchange constant between nearest neighbors) plane of a nearest neighbor lattice gas model an a simple cubic lattice with a free surface, and a potential (14) with $B = V_0 = 2.5J$. (b) The corresponding phase diagram in the grand-canonical ensemble $\mu' = (\mu - \mu_0)/J$ where μ_0 is the chemical potential at the bulk gas – liquid coexistence) Note that the adsorbate – substrate potential was cut off above the fourth layer, so that the curve for the layering transitions in the fifth and higher layers merge at the bulk coexistence curve (from Ref. 88)

Within the strong substrate regime the properties of adsorption systems appear to be very sensitive to even small changes in the relative strength of adsor-

bate – adsorbate and adsorbate – substrate interactions. Figures 6 and 7 show examples of phase diagrams resulting from Monte Carlo study of a lattice gas model with nearest neighbor adsorbate - adsorbate interaction but long range surface potential (given by eqn. (14) with $B = V_0$) [88]. In the case of strong substrate potential the film grows via a series of simple layering transitions involving condensation in one layer each. For a weaker surface potential one finds, however, a different sequence of layering transitions in which the first three layers condense together at low temperatures. This system shows also an example of a surface triple point at which the layering transitions of layers 1+2 and layer 3 coexist. Note that the critical point of the layering transition for layers 1+2 is considerably higher than the corresponding critical points for higher layers. This results from the enhanced effects of adsorbate - adsorbate interaction in the condensed two surface layers as compared with a single layer. Of course, even for a transition involving simultaneous condensation in several, but finite, number of layers the critical behavior corresponds to the universality class of a two-dimensional model, as the correlation length in the direction perpendicular to the surface stays finite.



Figure 7. The same as in Figure 4.15 but for a weaker substrate potential with $V_0 = 0.93J$ (from Ref. 88)

A sufficient decrease of substrate potential finally leads to the crossover from the strong to intermediate substrate regime. This crossover may be also induced by adding further neighbor (attractive) interactions between adsorbate particles [89]. Figure 8 shows a comparison of the phase diagram obtained for a simple model with the first nearest neighbor interaction with the phase diagrams corresponding to the model with added interaction between the third nearest neighbors.

4. FILMS ON SURFACES WITH FINITE CORRUGATION

As it was already demonstrated in section 2, atoms adsorbed on crystalline surfaces experience corrugated surface potentials. In the case of physisorption periodic variations of the gas – solid potential are usually small as compared with the adsorption energy and often are also smaller than or comparable with the thermal energy of the adsorbed atoms. In such situations the lattice gas models discussed in the previous section do not describe well the properties of adsorbed layers. Off lattice movement as well as out-of-plane excitations of adsorbed atoms give rise to many new phenomena that can not be included into the lattice gas formalism.



Figure 8. A comparison of the phase diagram for the lattice gas models with the first nearest neighbor interaction (part a) with the phase diagrams for the model with added second neighbor attractive interactions (parts b and c). Parts b and c show the results for $R = u_{2nn} / u_{nn} = 0.05$ and 0.08, respectively. Phase diagram in part a was taken from Ref. 88, while those shown in parts b and c from Ref. 89

In the case when the gas - solid potential exhibits periodic variations due to the lattice structure of the surface, a competition between the surface corrugation and the adsorbate - adsorbate interactions becomes a major factor determining the structure of adsorbed layers. In general, the adsorbate – adsorbate interaction tends to enforce the formation of the hexagonal close-packed (hcp) incommensurate solid phase in the monolayer film at low temperatures. On the other hand, the corrugated surface potential favors the formation of registered (or commensurate) structures. The actual structure of the film may be quite complicated and characterized by highly nonuniform spatial distribution of adsorbed atoms within the film. In the case of the most intensively studied adsorption on substrates with a hexagonal symmetry of the surface lattice, such a graphite [41,95-97], boron nitride [98,99], dense (111) plane of metal crystals (Pt, Cu, Ag) [13,100-103] and lamellar dihalides [60], both the commensurate and the incommensurate solid phases have the same symmetry and differ only by the spacing between neighboring atoms and by the orientation of the adsorbed layer lattice relative to the surface lattice [13,31,104-106]. In many cases the structure of the incommensurate phase can be described by the domain wall formalism [45,107].

In the case of adsorption on surfaces of a square and rectangular symmetry, such as low index planes $\{(100) \text{ and } (110)\}$ of the face centered crystals of various metals [14,108-112] or on the (100) plane of ionic regular crystals of MgO [91,113-117] and alkali halides [118-120], the situation looks quite different. Competing adsorbate – adsorbate and adsorbate – substrate interactions give rise to the formation of various registered superstructures [10], uniaxially ordered phases [121] as well as to various incommensurate phases [122].

Several important informations about the ordering in two-dimensional films formed on crystalline surfaces can be derived from the ground state calculations [52,67]. Bruch and Venables [67] considered the relation between the surface lattice and the adsorbed layer geometry in two-dimensional films adsorbed on crystals of different symmetry. They concentrated the discussion on the effects due to the corrugation potential and formulated explicit conditions for uniaxial registry. In that treatment the adsorbed film was assumed to be uniform in a sense that it was strictly two-dimensional and possessed a well defined lattice structure. The results obtained by Bruch and Venables must be considered as a sort of zeroth-order approximation only, since they did not attempt to minimize the system total energy, but rather focused on the calculations of the registry energy exerted by the surface corrugation potential only.

Some simple examples of the ground state calculations were reported by Patrykiejew et al. [52,53,69] in the case of adsorption on model (100) and (110) planes of atomic face centered cubic crystals, assuming that the adsorbed film forms a regular hexagonal lattice or simple registered phases such as (1×1) , $c(2\times2)$ and (2×1) . It was assumed that the adsorbate – adsorbate interaction potential u(r) is given by the Lennard-Jones function while $v_{2D}(\vec{\tau})$ was represented as

$$v_{2D}(\vec{\tau}) = \min[v(\vec{\tau}, z)] \tag{19}$$

with $v(\vec{\tau}, z)$ given by eq. (4).

In the case of an incommensurate hexagonal phase consisting of N atoms, the energy corresponding to a given distance between the first nearest neighbors (α_1) and to an also specified orientation of the adsorbed film with respect to the surface lattice (epitaxial rotation) [104-106] represented by the angle ϑ one has

$$e^{*}(\alpha_{1}^{*},\vartheta) = 12 \Big[C_{12}^{0} \big(\sigma^{*} / \alpha_{1}^{*} \big)^{12} - C_{6}^{0} \big(\sigma^{*} / \alpha_{1}^{*} \big)^{6} \Big] + \frac{1}{N} \sum_{i=1}^{N} v_{2D}^{*}(\vec{\tau}_{i}^{*})$$
(20)

where all energies are expressed in units of ϑ_{ee} and all lengths in units of α_1 .

This energy must be then minimized with respect to the both α_1^* and ϑ in order to find the stable configuration. One readily observes that in the thermodynamic limit $(N \to \infty)$ such a perfect, incommensurate, hexagonal phase has no preferred orientation [106] and the energy is given by

$$e^{*}(\alpha_{1}^{*}) = 12 \left[C_{12}^{0} \left(\sigma^{*} / \alpha_{1}^{*} \right)^{12} - C_{6}^{0} \left(\sigma^{*} / \alpha_{1}^{*} \right)^{6} \right] + v_{2D,0}^{*}$$
(21)

where $v_{2D,0}^*$ is the zeroth-order Fourier coefficient of $v_{2D}^*(\vec{\tau}^*)$ given by

$$v_{2D,0}^{*} = \frac{1}{a_{s}} \int_{a_{s}} v_{2D}(\vec{\tau}^{*}) d\vec{\tau}$$
(22)

where the integration is performed over the surface lattice cell of area a_s . The parameters C_{12}^0 and C_6^0 can be readily evaluated and their values depend on the assumed range of molecular interaction [123].

In the case of registered phases, in which all adsorbed atoms are located directly above the surface potential minima $\{\vec{\tau}_s^* = (0.5, 0.5a_2^*)\}$ we have

$$e_r^*(\sigma^*) = 8 \left[C_{12}^r \sigma^{*12} - C_6^r \sigma^{*6} \right] + v_{2D}^* \left(\vec{\tau}_s^* \right)$$
(23)

where the magnitudes of the parameters C_{12}^r and C_6^r depend on the assumed commensurate structure r [69].

Using such an approach the stability regions corresponding to the hcp and the registered (1×1) , $c(2\times2)$ (and (2×1) in the case of adsorption on the (110) plane of an fcc crystal) phases in adsorbed films formed on surfaces characterized by different size of the adsorbate atoms, given by σ^* , and different corrugation of the surface potential have been estimated (e.q., see Figure 9).

Of course, such calculations do not provide any exact solution to the problem of ground state properties of incommensurate phases as they ignore lattice distortions which arise from defects and local elastic relaxations, as discussed by Vives and Lindgård [106] as well as from the formation of domain-wall network structure [45].

To prepare a ground for a full appreciation of the surface corrugation effects on the finite temperature behavior of films adsorbed on crystalline surfaces, we now briefly discuss the properties of films formed on a "flat" noncorrugated surface. When the surface potential possesses a deep minimum at a certain preferred distance from the surface, z_0 , then the adsorbed film is essentially twodimensional at low temperatures. Deviations from planarity of adsorbed layer may be due to temperature rise [124,125] as well as may result from the formation of the second and higher layers [68].



Figure 9. Regions of stability of different surface phases for the Lennard-Jones particles adsorbed on the (100) plane of model fcc crystals deduced from the ground state calculations for the systems of the number density equal 1.0 (from Ref. 52)

The behavior of strictly two-dimensional Lennard-Jones systems has been intensively studied by various theoretical approaches [126-129] as well as by computer simulations [25,127,130-134]. In general, the phase diagram is quite well known. It has been found that it exhibits two-dimensional counterparts of all familiar states of matter in three-dimensional space: gas, liquid and solid (see Figure 9). The triple point temperature has been estimated quite accurately as equal to $T_{,*}^* = kT/\varepsilon = 0.40 \pm 0.015$ [127,134]. Existing estimations of the criti-

cal temperature for that system are much less conclusive [127,135] and obtained values range from about 0.5 to 0.56.

Another controversy about the properties of strictly two-dimensional Lennard-Jones system concerns the mechanism of melting. Already in the 1930's Peierls [136] argued that truly long-ranged positional order can not exist in twodimensional systems, so that two-dimensional crystalline order is impossible. This has been proved later by Mermin and Wagner [137]. In 1973 Kosterlitz and Thouless [29] proposed a theory dislocation-mediated melting for a twodimensional systems. That theory has been later developed further by Halperin and Nelson [30,138] and by Young [139]. From those theoretical works it follows that two-dimensional systems possess only quasi-long-renged positional order characterized by algebraic decay of the two-particle correlation function. The KTHNY theory predicts that melting in two-dimensions occurs via two continuous phase transitions. In the first transition, due to dissociation of dislocation pairs, the system looses the quasi-long-range positional order, but retains the quasi-long-range orientational order. This corresponds to the formation of the so-called hexatic phase. The second stage of melting is connected with the disclination-unbinding transition, occuring at higher temperature and leading to the formation of isotropic two-dimensional liquid.





The scenario predicted by the KTHNY theory is considerably altered by the presence of periodic substrate potential and the actual mechanism of melting

depends on the symmetry and the size of the substrate surface as well as on the amplitude of the periodic surface potential [138]. In general, surface corrugation is expected to wash-out the disclination-unbinding transition, and hence the melting becomes a one-step process. This transition may be continuous, as for the flat surface, or first-order. The only exception is the melting of a hexagonal adsorbate film on a square lattice characterized by weak corrugation of the adsorbate – substrate potential. In this case the theory proposed by Nelson and Halperin [30,138] predicts that the disclination-unbinding transition is replaced by an Ising-like transition. Thus, one expects to observe two liquid-like phases with different orientational symmetry.

There are also other theories [140-143] that predict the usual first-order melting in two-dimensional systems. The concept of first-order melting was also advocated by Abraham [25,144], who argued that the loss of positional order is negligible in real systems due to their limited, though macroscopic, size.

Computer simulation studies [25,133,134,144-146] as well as experimental data [147-151] do not provide an univocal answer to the problem of melting in two-dimensions. In real adsorption experiments the assumption of two-dimensionality of adsorbed film is seldom fulfilled. Out-of-plane movement of adsorbed particles is expected to be important factor which influences the properties and stability of all possible phases in monolayer films [68,123].

Monte Carlo simulations performed for a series of two-dimensional systems of Lennard-Jones particles with $\sigma^* = 0.9$ on surfaces with different corrugation [152] demonstrated that the mechanism of melting on corrugared surfaces is indeed considerably different from that predicted for a flat surface.

In order to determine the order and nature of the melting transition the behavior of the suitable bond-orientational order parameters [145] and their fourth-order cumulants for systems of different size were studied. The adlayers with a four-fold symmetry, as in the case of the both (1×1) and $c(2\times2)$ phases formed on the (100) plane of an fcc crystal, and the layers with a six-fold symmetry can be characterized by the following bond-orientational order parameters [152,153]

$$\Psi_{k} = \left| \frac{1}{N_{b}} \sum_{i} \sum_{j} \exp[ki\phi_{ij}] \right|$$
(24)

In order to detect axially ordered hexagonal phase one can define the bondorientational order parameter of the form

$$\Psi_6^{\epsilon} = \left| \frac{1}{N_b} \sum_i \sum_j \cos[6\phi_{ij}] \right|$$
(25)

In the above the first sum runs over the all molecules in the system, while the second sum is taken over the first shell of neighbors, N_b is the total number of "bonds" in the system and ϕ is the angle between the bond and the reference axis, taken to be the x-axis of the surface lattice.



Figure 11. Bond-orientational order parameters ψ_4 (part a) and ψ_6 (part b). The results shown in part (a) correspond to the systems with $\sigma^* = 1.20$, three different values of the corrugation parameter V_b and three different system sizes (shown in the figure) while the results shown in part (b) were obtained for $v_B = 0.6$ and three different system sizes (also shown in the figure) (from Ref. 153)

When the adsorbed layer is in a disordered fluid state, all the above defined bond-orientational order parameters should be equal to zero since all possible mutual orientations of "bonds" appear in the system with the same probability. In the case of registered phases of a square symmetry, ψ_4 is expected to be equal to unity, while the remaining order parameters ψ_6 and ψ_6^e should be equal to zero. In the hexagonal close packed phase ψ_{4} should approach zero while ψ_6 should be equal to unity. The behavior of ψ_6^e depends on the orientation of the adsorbed layer with respect to the surface lattice and may assume different values. When the film exhibits uniaxial registry but retains perfect hexagonal structure than $\psi_6^e = 1.0$. On the other hand, when the hexagonal arrangement is not perfect, we expect nontrivial behavior of ψ_6^e , as well as of ψ_4 and ψ_6 . Examples of the changes of ψ_4 and ψ_6 with temperature for adsorbed films formed on highly corrugated systems of different size are shown in Figure 11. It is quite clear that in all cases the adsorbed layers exhibit square symmetry at low temperatures and undergo rather abrupt, though continuous, disordering as the temperature increases. The absence of any finite size effects is a clear evidence that no longwavelength fluctuations develop. The finite size effects are only manifested in the behavior of residual ψ_6 (cf. Figure 11b), but this merely reflects gradual approach towards the thermodynamic limit.

It is well known [154,155] that in the case of a second order phase transition the fourth-order cumulants of the order parameter reach a trivial limit of 2/3 at the temperatures well below the transition point and zero at the temperatures well above the transition point. At the transition temperature the cumulants for different system sizes should reach a common nontrivial intersection point U^* with the magnitude of U^* depending on the universality class of the phase transition. The results presented in figure 12 seem to confirm the predictions of the KTHNY theory. At the temperature $T^* \approx 0.4$ the bond-orientational order parameters ψ_6 and ψ_6^* both exhibit a sudden, though small, drop.



Figure 12. Bond-orientational order parameters ψ_6 and ψ_6^e for the two-dimensional system of 894 particles with $\sigma^* = 0.9$ adsorbed on the surface of low corrugation, characterized by $V_b = 0.1$, and the size of 32×28 surface unit cells as well as the fourth-order cumulants $U_6(L)$ for different system sizes obtained from Monte Carlo simulation (from Ref. 152)

Thus, above that temperature the system retains a considerable orientational order. According to the KTHNY theory this first transition, due to dissociation of dislocation pairs, transforms the solid phase into the hexatic phase. Then a second transition occurs at the temperature of about 0.485, which leads to the loss of orientational order in the system. The behavior of U_L , also depicted in Figure 12, shows that the cumulants for different systems sizes do show a

common intersection at U^* close to 0.61. This value of the cumulant fixed point correspond to the universality class of the Ising model [154].

Real adsorption systems usually show some effects of out-of-plane motion of adsorbed particles, even at low temperatures. The increase of the pressure, or the chemical potential, for the monolayer film may induce many new phenomena. What actually happens to the film depends crucially on the strength of the adsorbate – adsorbate and the adsorbate – adsorbent interaction, as already discussed in sec. 2. Also the surface corrugation is expected to be a very important factor influencing the film behavior.

Possible scenarios may include the appearance of layering transitions, formation of compact three-dimensional crystallites, promotion of the second layer due to melting and disordering of the first adsorbed layer as well as simple desorption of particles due to increase in their kinetic energy. Also, the structure of adsorbed layers adjacent to the substrate surface may change upon the formation of higher layers, so that various commensurate – incommensurate transitions may occur in the film.

The problem of monolayer stability is closely related to the wetting of a substrate by an adsorbed film. In the resent paper by Phillips [156], is was demonstrated via the molecular dynamics simulation and analytic solution of the elastic continuum models that three different mechanisms may be responsible for an instability of the adsorbed monolayer and the promotion of the second, as well as higher, layers. In a strongly adsorbed film, the promotion of the second layer, under the specified thermodynamic conditions of temperature and pressure, occurs mostly due to migration of the atoms located at the edges of adsorbed islands of a compact two-dimensional solid layer. This process may be also accompanied by, much more rarely occuring, movement of individual atoms from the interior of the island to the second layer, if they happen to gain enough kinetic energy. These two mechanisms were observed also in the case of melting in dense monolayer films as will be discussed later. The third possible mechanism leading to the promotion of higher layers may be a sudden promotion of groups of adsorbed atoms due to the response to structural instability in the highly compressed solid layer. This last mechanism is most likely to occur in dense and relatively weakly adsorbed films in which stresses and strains are of particular importance.

Of course, the above mentioned effects are most likely to occur in adsorbed films formed on rather weakly corrugated surfaces, since such systems are most likely to form islands of a high density solid phase. In the case of strongly corrugated surfaces, on which the registered films are usually found, the promotion of the higher layers is not likely to occur. It can be rather expected that only a sufficient increase in the temperature may induce disordering which is accompanied and/or followed by desorption. The stability of the registered structures in the first layer appears to be quite sensitive to even small changes of the surface corrugation as well as to the density changes in the film, as it was recently demonstrated by Patrykiejew et al. [69]. An interesting phenomenon observed in adsorbed films studied by Monte Carlo simulation is the reconstruction of the first adsorbed layer due to the formation of the second layer. Namely, it was found that, in some cases, the dense monolayer films formed on a sguare lattice assume incommensurate structure of hexagonal symmetry, while the appearance of the second layer causes a gradual restructuring of the first layer, which recovers the ordered epitaxial structure of a square symmetry (see Figure 13). Thus, the appearance of the second layer exerts a force which pushed the adsorbed atoms from the first layer back into the registry positions.

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Figure 13. Snap shot configurations for the adsorbed layer of Lennard-Jones particles of $\sigma^* = 0.8$ on the (100) plane of the model fcc crystal with the corrugation parameter $V_b = 0.9$ recorded at the temperature $T^* = 0.02$ and the total film number density equal to $\rho_n = 1.5625$ (part a) and 2.0 (part b). Particles located in the first layer are represented by open circles while those from the second layer by filled circles (from Ref. 69)

Figure 14 shows the phase diagram derived from the Monte Carlo simulation for another system, which exhibits the registered (1×1) and the incommensurate structures in the monolayer region and also incommensurate second layer.



Figure 14. Phase diagram for the Lennard-Jones adsorbed bilayer film formed on the (100) plane of fcc crystal characterized by the corrugation parameter $V_b = 0.8$. Part a shows the phase diagram in the plane (ρ_n, T^*) . Filled points are the results of grand canonical Monte Carlo calculations, while stars and diamonds correspond to the canonical ensemble calculations. The triple line of the solid – liquid – gas coexistence in the second layer is shown as a broken vertical line. Part b shows the phase diagram in the (μ^*, T^*) plane derived from the grand canonical ensemble Monte Carlo simulation. The gas – commensurate (1×1) phase transition points are shown as filled points, the commensurate – incommensurate transition points in the first layer are represented by open goints, while the layering transition points in the second layer are marked by open diamonds. The location of the gas – (1×1) phase transition at the zero temperature was obtained from the ground state calculations, while the locations of the commensurate and layering transitions at the zero temperature were estimated by extrapolation of the results obtained for finite temperatures. (From Ref. 68)



Figure 15. The heat capacity curves for the Lennard-Jones adsorbed films of different density (shown in the figure) formed on the (100) plane of fcc crystal characterized by the corrugation parameter $V_b = 0.8$. The peaks at the temperature of about $T^* = 0.4$ obtained for the systems with the two highest values of the density correspond to the triple-point melting of the second layer, while the remaining peaks result from the melting of the monolayer incommensurate solid phase (from Ref. 68)

The data shown in Figure 15 demonstrate that the temperature of the melting transition of the incommensurate monolayer solid phase moves towards higher values when the density of that phase increases. Only for the films which exhibit the formation of the second layer the melting temperature is constant and equal to about 0.5. Ouite similar effect was found experimentally for nitrogen adsorbed on graphite [44]. It was demonstrated that it is connected with a different mechanism of the melting transition in submonolayer and dense monolayer solid films. Submonolayer solid does not occupy the entire surface but rather forms high density islands which coexist with a dilute phase. Upon melting the more or less uniform fluid phase is formed and spreads over the entire surface. This can not happen in already dense monolayer since there is not enough space for the fluid phase. The only possibility for the liquid monolayer to appear is the decrease of the density in the first layer by the promotion of the second layer. This mechanism was found in the computer simulation studies for methane films on graphite [63] and for argon films on (100) MgO [157]. Note that this last system is characterized by the square symmetry of the surface lattice. In the case of model systems discussed above, it was also found that submonolayer films melt without any effects due to the promotion of the second layer, while the melting of a dense monolayer solid is accompanied by the transfer of particles from the first to the second layer (see Figure 16).





Although the above discussion presented only some selected examples of experimental and theoretical studies of ordering phenomena in adsorbed films, it demonstrated that the structure and the thermodynamic properties of adsorption systems are very sensitive to the details of the molecular interactions operating in such systems. In particular, we tried to show that one of the most important factors that determine the behavior of adsorbed layers is the corrugated surface potential and the symmetry of the surface lattice. Also, we attemped to show that computer simulation methods are powerful tools, which allow to get important new insights into the physics of adsorption systems as well as lead to the results allowing for a better understanding of several experimentally observed phenomena.

5. REFERENCES

- [1] Dash J. G., Films on Solid Surfaces, Academic Press, New York, 1975.
- [2] Sinha S. K. (Ed.), Ordering in Two-Dimensions, North-Holland, Amsterdam, 1980.
- [3] Dash J. G., Ruvalds R. (Eds.), Phase Transitions in Surface Films, Plenum, New York, 1980
- [4] Taub H., Torzo G., Lauter H. J., Fain S. C., Jr. (Eds.), Phase Transitions in Surface Films 2, Plenum, New York, 1991.
- [5] Binder K., Landau D. P., in Advances in Chemical Physics, Ed.:
 K. P. Lawley, Wiley, Chichester, 1989, p91.
- [6] Taub H., Carneiro K., Kjems J. K., Passell L., McTague J. P., Phys. Rev. B, 16, 4551 (1977).
- [7] Clarke L. J., Surface Crystalography, Wiley, Chichester, 1985.
- [8] Jons F., Strozier J. A., Jr. Yang W. S., Rep. Prog. Phys., 45, 527 (1982).
- [9] Heinz K., Rep. Prog. Phys., 58, 637 (1995).
- [10] Behm R. J., Christmann K., Ertl G., Surf. Sci., 99, 320 (1980).
- [11] Imbihl R., Behm R. J., Christmann K., Ertl G., Matsushima T., Surf. Sci., 117, 257 (1982).
- [12] Grunze M., Kleban P. H., Unertl W. N., Rys F. S., Phys. Rev. Lett., 51, 582 (1983).
- [13] Leatherman G. S., Diehl R. D., Karimi M., Vidali G., Phys. Rev. B, 56, 6970 (1997).
- [14] Glachant A., Jaubert M., Bienfait M., Boato G., Surf. Sci., 115, 219 (1981).
- [15] Steele W. A., *The Interaction of Gases with Solid Surfaces*, Pergamon Press, New York, 1974.
- [16] Kern K., Comsa G., in Advances in Chemical Physics, Ed.: K. P. Lawley, Wiley, Chichester, 1989.
- [17] Morck R., Shahal O., Surf. Sci. Lett., 177,, L963 (1986).
- [18] Sullivan N. S., Vaissiere J. M., Phys. Rev. Lett., 51, 658 (1983).
- [19] Bretz M., Dash J. G., Hickernell D. C., McLean E. O., Vilches O. E., Phys. Rev. A, 8, 1589 (1973).
- [20] Lysek M., Day P., LaMadrid M., Goodstein D., Rev. Sci. Instrum., 63, 5750 (1992).
- [21] Jensen F. T., Palmer R. E., Surf. Sci., 233, 269 (1990).
- [22] Binder K. (Ed.), The Monte Carlo Method in Statistical Physics, Springer, Berlin, 1979.
- [23] Binder K. (Ed.), Applications of the Monte Carlo Method in Statistical Physics, Springer, Berlin, 1984.
- [24] Allen M. P., Tildesley D. J., Computer Simulation of Liquids, Clarendon Press, Oxford, 1987.

- [25] Abraham F. F., Phys. Rep., 80, 339 (1981).
- [26] Selke W., Phys. Rep., 170, 213 (1988).
- [27] Allen M. P., Tildesley D. J. (Eds.), Computer Simulation in Chemical Physics, Kluwer, Dortrecht, 1993.
- [28] Landau D. P., in Monte Carlo and Molecular Dynamics of Condensed Matter Systems, Eds. K. Binder, G. Ciccotti, Italian Physical Society, Bologna, 1996.
- [29] Kosterlitz M., Thouless P. J., J. Phys. C, 6, 1181 (1973).
- [30] Halperin B. I., Nelson R. D., Phys. Rev. Lett., 41, 121 (1978).
- [31] Novaco A. D., McTague J. P., Phys. Rev. Lett., 38, 1286 (1977).
- [32] Ostlund S., Berker A. N., Phys. Rev. B, 21, 5410 (1980).
- [33] Haldane F. D. M., Villain J., J. Phys., (Paris) 42, 1673 (1981).
- [34] Pandit R., Schick M., Wortis M., Phys. Rev. B, 26, 5112 (1982).
- [35] Dietrich S., in Phase Transitions and Critical Phenomena, vol. 12, Eds.: C. Domb, J. L. Lebowitz, Academic Press, London, p. 1.
- [36] Binder K. in Cohesion and Structure of Surfaces, Eds.: F. R. de Boer, D. G. Pettifor, Elsevier, Amsterdam, 1995, p. 121.
- [37] Thomy A., Duval X., Colloq. Int. CNRS, Nancy, 132, 81 (1965).
- [38] Thomy A., Duval X., J. Chim. Phys. Chim. Biol., 66, 1966 (1969).
- [39] Thomy A., Duval X., J. Chim. Phys. Chim. Biol., 66, 286, 1101 (1969).
- [40] Thomy A., Duval X., Hebd C. R., Seances Acad Sci., 259, 407 (1964).
- [41] Thomy A., Duval X., Regnier J., Surf. Sci. Rep., 1, 1 (1981).
- [42] Bak P., Rep. Prog. Phys., 45, 587 (1982).
- [43] Chan M. H. W., in Ref. 4, p.1
- [44] Marx D., Wiechert H., in Adv. Chem. Phys., 95, 213 (1996) and references cited therein.
- [45] Villain J., Surf. Sci., 97, 219 (1980).
- [46] Shiba H., J. Phys. Soc. (Japan) 46, 1852 (1979).
- [47] Chang S.-L., Thiel P. A., J. Chem. Phys., 88, 2071 (1988).
- [48] Wang G. C., Lu T. M., Legally M. G., J. Chem. Phys., 69, 479 (1978).
- [49] Meichel T., Suzanne J., Girard C., Girardet C., Phys. Rev. B, 38, 3781 (1988).
- [50] Glachant A., Bardi W., Surf. Sci., 87, 187 (1979).
- [51] Steele W. A., Surf. Sci., 36, 317 (1973).
- [52] Patrykiejew A., Sokołowski S., Zientarski T., Binder K., J. Chem. Phys., 102, 8221 (1995).
- [53] Patrykiejew A., Sokołowski S, Zientarski T., Binder K., J. Chem. Phys., 108, 5068 (1998).
- [54] Chen J. R., Gomer R., Surf. Sci., 94, 456 (1980).
- [55] Drakora D., Doyen G., Trentini F. V., Phys. Rev. B 32, 6399 (1985).
- [56] Müller J. E., Phys. Rev. Lett., 65, 3021 (1990).
- [57] Bruch L. W., Wei M. S., Surf. Sci., 100, 481 (1980).

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- [58] Wei M. S., Bruch L. W., J. Chem. Phys., 75, 4130 (1981).
- [59] Bruch L. W. in *Phase Transitions in Surface Films 2*, Eds.: H. Taub, G. Torzo, H. J. Lauter, S. C. Fain, Jr., Plenum Press, New York, 1991, p. 67.
- [60] Larher Y., in Surface Properties of Layered Structures, Ed.: G. Benedek, Kluwer, Netherlands, 1992, p. 261.
- [61] Kim H.-Y., Steele W. A., Phys. Rev. B, 44, 8962 (1991).
- [62] Hruska C. D., Phillips J. M., Phys. Rev. B, 37, 1988 (1988).
- [63] Phillips J. M., Hruska C. D., Phys. Rev. B, 39, 5425 (1989).
- [64] Phillips J. M., Langmuir, 5, 571 (1989).
- [65] Phillips J. M., Story T. R., Phys. Rev. B, 42, 6944 (1990).
- [66] Phillips J. M., Shrimpton N., Phys. Rev. B, 45, 3730 (1992).
- [67] Bruch L. W., Venables J. A., Surf. Sci., 148, 167 (1984).
- [68] Patrykiejew A., Sokołowski S., Zientarski T., Binder K., Surf. Sci., 421, 308 (1999).
- [69] Patrykiejew A., Sokołowski S., Zientarski T., Binder K., Langmuir, 15, 3642 (1999).
- [70] Park R. L., Madden H. H., Surf. Sci., 11, 188 (1968).
- [71] Aubry S. in Solitons in Condensed Matter Physics, Springer, Heidelberg, 1978, p. 264.
- [72] den Nijs M. in Phase Transitions and Critical Phenomena, vol. 12, Eds.: C. Domb, J. L. Lebowitz, Academic Press, London, 1988, p. 219.
- [73] Patrykiejew A. in Adsorption on New and Modified Inorganic Sorbents, Studies in Surface Science and Catalysis, vol. 99 (Eds. A. Dąbrowski and V. A. Tertykh), Elsevier, Amsterdam, 1996.
- [74] Estrup P. J. in *The Structure and Chemistry of Solid Surfaces*, Ed. G. A. Somorjai, Wiley, New York, 1969.
- [75] Taylor D. E., Williams E. D., Parc R. L., Bertelt N. C., Einstein T. L., Phys. Rev. B, 32, 4653 (1985).
- [76] Tu Y., Blakely J. M., Surface Sci., 85, 276 (1979).
- [77] Doyen G., Ertl G., Plancher M., J. Chem. Phys., 62, 2957 (1975).
- [78] Weeks S. P., Rowe J. E., J. Vac. Sci. Technol., 16, 470 (1979).
- [79] Wei D.-H., Sketton D. C., Kevan S. D., J. Chem. Phys., 105, 7808 (1996).
- [80] Bak P., Kleban P., Unertl W. N., Ochab J., Akinci G., Bartelt N. C., Einstein T. L., Phys. Rev. Lett., 54, 1539 (1985).
- [81] Bartelt N. C., Roelofs L. D., Einstein T. L., Surface Sci. Lett., 221, L750 (1989).
- [82] Ashkin J., Teller E., Phys. Rev., 64, 178 (1943).
- [83] de Oliviera M. J., Griffiths R. B., Surface Sci., 71, 687 (1978).
- [84] Kim I. M., Landau D. P., Surface Sci., 110, 415 (1981).
- [85] Ebner C., Phys. Rev. B, 28, 2890 (1983).
- [86] Binder K., Landau D. P., Phys. Rev. B, 37, 1745 (1988).

- [87] Ebner C., Phys. Rev. A, 22, 2776 (1980).
- [88] Patrykiejew A., Landau D. P., Binder K., Surface Sci., 238, 317 (1990).
- [89] Kruk M., Patrykiejew A., Sokołowski S., Thin Solid Films, 238, 302 (1994).
- [90] Prasad A., Weichman P. B., Phys. Rev., 57, 4900 (1998).
- [91] Coulomb J. P. in *Phase Transitions in Surface Films 2*, Eds.: H. Taub, G. Torzo, H. J. Lauter, S. C. Fain, Jr., Plenum Press, New York, 1991, p. 113.
- [92] Binder K., Landau. D. P, Surf. Sci., 108, (1981).
- [93] Dietrich S., Schick M., Phys. Rev. B, 33, 4952 (1986).
- [94] Forgacs G., Lipowsky R., Niewenhuizen Th. M., in Phase Transitions and Critical Phenomena, vol. 14, Eds. C. Domb, J. L. Lebowitz, Academic Press, London, 1991, p. 135.
- [95] Larher Y., J. Chem. Phys., 68, 2257 (1978).
- [96] Chinn M. D., Fain S. C., Phys. Rev. Lett., 39, 146 (1977).
- [97] Johnson D. E., Phillips J. M., Larese J. Z., Phys. Rev. B, 56, 6462 (1997).
- [98] Regnier J., Thomy A., Duval X., J. Coll. Interface Sci., 70, 105 (1979).
- [99] Bockel C., Thomy A., Duval X., Surface Sci., 90, 109 (1979).
- [100] Unguris J., Bruch L. W., Webb M. B., Phillips J. M., Surface Sci., 114, 219 (1982).
- [101] Gottlieb J. M., Phys. Rev. B, 42, 5377 (1990).
- [102] Tully J. C., Surface Sci., 226, 461 (1991).
- [103] Diehl R. D. in Phase Transitions in Surface Films 2, Eds. H. Taub, G. Torzo, H. J. Lauter, S. C. Fain, Jr., Plenum, New York, 1991, p. 97.
- [104] McTague J. P., Novaco A. D., Phys. Rev. B, 19, 5299 (1979).
- [105] Gray F., Bohr J. in Phase Transitions in Surface Films 2, Eds. H. Taub, G. Torzo, H. J. Lauter, S. C. Fain, Jr, Plenum, New York, 1991, p. 83.
- [106] Vives E., Lindgård P. A., Phys. Rev. B, 47, 7431 (1993).
- [107] Villain J. in Ordering in Strongly Fluctuating Condensed Matter Systems, Ed.: T. Riste, Plenum, New York, 1980, p. 221.
- [108] Palmberg P. W., Surf. Sci., 25, 598 (1971).
- [109] de Beauvais C., Rouxel D., Mutaftschiev B., Bigeard B., Surf. Sci., 272, 73 (1992).
- [110] Chesters M. A., Hussain M., Pritchard J., Surface Sci., 35, 161 (1973).
- [111] Ramsayer C., Girardet C., Zeppenfeld P., George J., Büchel M., Comsa G., Surface Sci., 313, 251 (1994).
- [112] Kern K., David R., Zeppenfeld P., Palmer R., Comsa G., Solid State Commun., 61, 391 (1987).

- [113] Coulomb J. P., Sullivan T. S., Vilches O. E., Phys. Rev. B, 30, 4753 (1984).
- [114] Bienfait M., Coulomb J. P., Palmari J. P., Surface Sci., 182, 557 (1987).
- [115] Coulomb J. P., Madih K., Croset B., Lauter H. J., Phys. Rev. Lett., 54, 1536 (1985).
- [116] Sidoumou M., Angot T., Suzanne J., Surface Sci., 272, 347 (1992).
- [117] Ferry D., Suzanne J., Surface Sci., 345, L19 (1996).
- [118] Hayakawa T., Bull. Chem. Soc. Japan, 30, 124, 236, 243, 332, 337, 343 (1957).
- [119] Heidberg J., Kampshoff E., Schönekäs O., Stein H., Weiss H., Ber. Bunsenges. Phys. Chem., 94, 118 (1990).
- [120] Dericbourg J., Surface Sci., 269/270, 1157 (1992).
- [121] Gottlieb J. M., Bruch L. W., Phys. Rev. B, 44, 5759 (1991).
- [122] Ramseyer C., Hoang P. N. M., Girardet C., Surface Sci., 265, 293 (1992).
- [123] Patrykiejew A., Sokołowski S., Binder K., Surf. Sci. Rep. (in press)
- [124] Monson P. A., Cole M. W., Taigo F., Steele W. A., Surface Sci., 122, 401 (1982).
- [125] Patrykiejew A., Sokołowski S., Thin Solid Films, 128, 171 (1985).
- [126] Monson P. A., Steele W. A., Henderson D., J. Chem. Phys., 74, 6431 (1981).
- [127] Barker J. A., Henderson D., Abraham F. F., Physica, 106A, 226 (1981).
- [128] Klein J. R., Cole M. W., Faraday Discuss. Chem. Soc., 80, 71 (1985).
- [129] Cuadros F., Mulero A., Chem. Phys., 177, 53 (1993).
- [130] Tsien F., Valleau J. P., Molec. Phys., 27, 177 (1974).
- [131] Toxvaerd S., Molec. Phys., 29, 273 (1975).
- [132] Toxvaerd S., Phys. Rev. A, 24, 2735 (1981).
- [133] Phillips J. M., Bruch L. W., Murphy R. D., J. Chem. Phys., 75, 5097 (1981).
- [134] Tabochnik J., Chester G. V., Phys. Rev. B, 25, 6778 (1982).
- [135] Rovere M., Heermann D. W., Binder K., J. Phys.: Condens. Matter 2, 7009 (1990).
- [136] Peierls R., Ann. Inst. Henri Poincaré, 5,, 177 (1935).
- [137] Mermin N. D., Wagner H., Phys. Rev. Lett., 17, 1133 (1966).
- [138] Nelson R. D., Halperin B. I., Phys. Rev. B, 19, 2457 (1979).
- [139] Young A. P., Phys. Rev. B, 19, 1855 (1979).
- [140] Chui S. T., Phys. Rev. Lett., 48, 933 (1982); Phys. Rev. B, 28, 178 (1983).
- [141] Ramakrishnan T. V., Phys. Rev. Lett., 48, 541 (1982).
- [142] Kleinert H., Phys. Lett. A, 95, 381 (1983).
- [143] Joos B., Duesbery M. S., Phys. Rev. Lett., 55, 1997 (1985).

- [144] Abraham F. F., Phys. Rev. Lett., 44, 463 (1980).
- [145] Strandburg K. J., Rev. Mod. Phys., 60, 161 (1988).
- [146] Udink C., van der Elsken J., Phys. Rev. B, 35, 279 (1987).
- [147] Heiney P. A., Stephans P. W., Birgeneau R. J., Horn M. P., Moncton D. E., Phys. Rev. B, 28, 6416 (1983).
- [148] Nagler S. E., Horn P. M., Rosenbaum T. F., Birgeneau R. J., Sutton M., Mochrie S. G. J., Moncton D. E., Clarke R., *Phys. Rev. B*, 32, 7373 (1983).
- [149] McTague J. P., Als-Nielsen J., Bohr J., Nielsen M., Phys. Rev. B, 25, 7765 (1982).
- [150] Migone A. D., Li Z. R., Chan M. H. W., Phys. Rev. Lett., 53, 1133 (1984).
- [151] Litzinger J. A., Stewart G. A., in Ordering in Two Dimensions, Ed. S. K. Sinha, North-Holland, Amsterdam, 1980, p. 147.
- [152] Patrykiejew A., Zientarski T., Binder K., Acta Phys. Polon., 89, 735 (1996).
- [153] Patrykiejew A., Sokołowski S., Zientarski T., Langmuir, 13, 1036 (1997).
- [154] Binder K., Z. Phys. B, 43 (1981) 119.
- [155] Vollmayr K., Reger J. D., Scheucher M., Binder K., Z. Phys. B, 91, 113 (1993).
- [156] Phillips J. M., Phys. Rev. B, 51, 7186 (1995).
- [157] Alavi A., McDonald I. R., Mol. Phys., 69, 703 (1990).

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