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TWO DIMENSIONAL PHASE EQUILIBRIA AT SURFACES

J.M. BLAKELY

Materials Science and Engineering, Cornell University, Ithaca, NY 14853-1501, U.S.A.

Abstract

This paper provides a brief discussion of some current experimental work on phase transitions at free surfaces. Examples are used to illustrate work in the areas of surface reconstruction, roughening, atomic step coalescence, and transformations of adsorbed and segregated layers. All of these surface phenomena are likely to have counterparts at internal boundaries.

I. Introduction:

The interfaces discussed in this paper are those between a crystal and vacuum or a low pressure vapor. These 'external' surfaces have been studied much more extensively than those between condensed phases. From the experimentalist's viewpoint they are more accessible and the wealth of data now available has encouraged theorists to make major efforts in computation \(1,2\) of surface properties. A wide variety of surface phase transitions have been documented and some rather sophisticated models of these phenomena exist in the literature. In many respects the modelling of surface phase transitions is more advanced than that for 3-dimensional systems mainly due to the mathematical simplifications introduced by the reduced dimensionality.

In this paper a few examples of surface phase transitions are described. In most cases it is easy to imagine similar or related phenomena occurring at internal boundaries. The phase transitions discussed involve (i) surface reconstructions, (ii) atomic roughening, (iii) atomic step clustering and faceting, (iv) adsorbed overlayer superlattices, (v) segregated layers on alloy crystals and (vi) 2-dimensional adsorbed alloys.

II. Stability and Coexistence of Surface Phases

The stable structures that exist at a surface are those which are in equilibrium with the bulk and vapor phases as well as with each other. It is indeed rare that this state of thermodynamic equilibrium is achieved so that the majority of surface phases observed are in some respect metastable. This is of course also true of bulk phases. Transitions among surface phases may be limited
by nucleation or atom transport processes while volume diffusion, adsorption and desorption rates may limit communication between the surface and the neighboring bulk phases. The surface region may therefore behave in extreme cases either as an open or a closed system in the thermodynamic sense. In the first case chemical potentials can be controlled through vapor pressures or alloy composition while in the second case the surface chemical potentials will generally differ from those in the bulk phases and will be determined by the (fixed) average density and composition of the surface region. Examples of both extreme situations will be mentioned later in the paper. While both open and closed surface systems may be described thermodynamically, intermediate conditions are not so readily analysed.

For surface (and interfacial) phases, pressure and volume are not useful variables. Different conventions for defining surface thermodynamic quantities involve somewhat arbitrary assignments to the surface volume, a problem that clearly arises from the fact that the physical extent of the surface phase may be comparable to that of the transition region that separates it from the bulk. The surface tension, \(\gamma\), and area, \(A\), are, however, well defined quantities and essentially replace pressure and volume for surface phases. The conditions for equilibrium coexistence of surface and bulk phases involve uniformity of temperature, chemical potentials, pressure for bulk phases and surface tension for surface phases, i.e. for a set of surface phases I, II, III, ... we must have \(\gamma_I = \gamma_{II} = \gamma_{III} \ldots\). The ranges of stability for surface phases might then be represented on \(\gamma-T\)-composition phase diagrams with a phase rule similar to that for bulk phases, i.e.,

\[
W = n + 2 - \chi
\]

where \(W\) is the number of parameters that can be varied independently (i.e., the variance) and still maintain \(\chi\) phases in an \(n\) component system. Phase diagrams of this type have indeed been obtained for Langmuir-Blodgett monolayer films on liquids but for solid systems, surface tension is generally a quantity that is both difficult to control and to measure. The stability of surface phases may be represented on a variety of alternative diagrams. For example, for the phases of a one-component layer adsorbed on an 'inert' substrate and in equilibrium with a vapor, vapor pressure \(P\) and \(T\) would be convenient variables; figure (11) \(7\) shows an example of such a diagram. The surface phases of an alloy crystal in which surface to bulk equilibrium is achieved through diffusion could similarly be represented on a diagram of bulk composition versus \(T\); figure (10) \(8\) shows such an example. The 2-phase coexistence curves for these open system phase diagrams can in fact be described in a formal way by Clapeyron type equations \(4,9\), for example for a one component layer in equilibrium with a
vapor, the equation
\[
\frac{\ln p}{(1/T)} = \frac{1}{R} \left[ q_{\text{ads}} - q_{\text{tr}} \frac{e_{\text{II}}}{e_{\text{I}} - e_{\text{II}}} \right]
\]

(2)
describes the coexistence of two surface phases I and II as a function of gas pressure and temperature. \(e_I\) and \(e_{\text{II}}\) are the fractional occupancies (or coverages) of possible adsorption sites in the two phases, \(q_{\text{ads}}\) is the isosteric heat of adsorption for phase I and \(q_{\text{tr}}\) the heat of transformation from I to II; both of these heats will be coverage dependent. (For the alloy segregation case \(P\) would be replaced by atomic fraction \(\chi\)).

For closed adsorbed layers, the chemical potentials are not fixed by some bulk reservoir but the average coverages can be adjusted experimentally; it is then more convenient to represent the ranges of stability of different phases on temperature-composition-coverage diagrams (10), (Figure (1)). Figure (12) is an example of a \(T-\theta\) diagram for a one component adsorbed layer i.e. fixed composition while figure (13) (12) gives a \(T\)-composition diagram for a binary adsorbed layer at fixed coverage. Further comments on these diagrams will be made later.

![Figure 1. Axes for phase diagram describing a binary 2-dimensional adsorbed layer. The conventional diagram for a single component layer corresponds to the plane \(\chi=0\) or 1. The dashed plane corresponds to a section at constant total coverage; this section should have features similar to those of conventional diagrams of 3-dimensional binary alloys.](image)

III. Structural Transitions of Clean Surfaces

The atomic structure of crystal-vacuum interfaces has been studied by a fairly impressive array of experimental methods including scattering of electrons (13), x-rays (14), atoms or molecules (15) and ions (16) as well as high resolution techniques of field ion (17) and scanning tunneling microscopies. At clean surfaces the atomic structure often differs from that expected for an ideally terminated crystal. Examples of these deviations are briefly discussed.
(i) Surface Reconstruction

Several types of atomic rearrangements in the topmost layer(s) of a crystal from those in corresponding bulk planes have been identified. In many cases there is an overall expansion or contraction of the interplanar spacings in the surface layers normal to the surface; the measurements of such contractions requires very careful scattering measurements and analyses (13). The formation of surface superlattices is generally easier to establish through the appearance of extra reflections in surface diffraction patterns (19) and it is these surfaces with longer period structures which are referred to as reconstructed. Among the most studied surfaces showing reconstruction are the (100) and (111) surfaces of Si (20,21). Models of the ideal and (2x1) reconstructed (100) surface of Si are depicted in Figure (2) (22,23). The formation of the (2x1) is

![Figure 2a. Several models for 2x1 reconstructed Si(100) surface. Surface atoms are shown as open circles and second layer atoms as dark circles. The models shown are: (a) ideal, unrelaxed surface; (b) symmetric (or covalent) dimer; (c) and (d) vacancy models; (e) conjugated-chain model; (f) "double" conjugated-chain model in which every atom is fourfold coordinated. [After Chadi, J. Vac. Sci. Technol. 16, 1291 (1979)]]

![Figure 2b. Asymmetric (or ionic) dimer geometry. Side view is schematic and is not drawn to scale. [From Chadi: J. Vac. Sci. Technol., 16, 1291 (1979)]]
attributed to the formation of surface dimers with an accompanying decrease in surface dangling bond density from 2 to 1 per surface atom. The lowest energy configuration of the dimers is asymmetrical (24) (Figure (3)) and higher order reconstructions observed in LEED have been attributed to the sense of this asymmetry (25). Very clear evidence exists in scanning tunneling microscope images (23) for the occurrence of dimers on this (100) surface. In addition to these and other experimental observations very extensive tight binding calculations have been made on the energies associated with these structures. Some of these results are summarized in Figure (3) (25, 26). The energy of the (2x1) phase is reduced relative to the unreconstructed (1x1) by \( \approx 0.85 \) eV per surface atom while the higher order (4x2) phase involves a further reduction of only \( \approx 0.03 \) eV (25). These energies are qualitatively consistent with the experimental observations that the (2x1) reconstruction persists to high temperatures while the (4x2) phase disorders to (2x1) near room temperature.

The Si(111) surface also exhibits reconstructed phases. The (2x1) observed on cleaved surfaces is metastable and transforms to the slightly lower energy (7x7) surface on annealing; the transition between (7x7) and (1x1) is in the region of 850°C. The structures of these phases have been the subject of a very large experimental (29) and theoretical effort and well supported models of the reconstructed phases now exist.

(ii) The Roughening Transition

On an ideal (or reconstructed) surface at low temperatures the coordinates of all surface atoms can be predicted from those of one unit cell. However, as temperature is increased and point and other defects are spontaneously created due to the accompanying increase in entropy the surface may become diffuse or rough so that correlation in the normal coordinates of pairs of outermost atoms diminishes. For a surface of infinite lateral extent the width of the crystal vacuum interface would diverge as the critical roughening temperature is approached. Burton, Cabrera, and Frank (30) developed a theory for this roughening transition based on an adaptation of the Ising model and more recent analytical descriptions (31, 32) are extensions of this work. Figure (4) (31) is a view of the equilibrium structure of a (100) surface obtained using Monte Carlo methods, based on a nearest neighbour bonding model, at various reduced temperatures. So
far there have been few direct measurements of spontaneous surface roughening. It is generally agreed that the close packed surfaces of most 'simple' crystals do not show appreciable roughening below the melting point. However the theory (31) strongly suggests that vicinal and high index planes with lower average surface coordination may exhibit significant roughening. Recent measurements of the intensity profiles of He diffraction beams (33,34) over a range of temperatures have been used to extract parameters characterizing surface roughness. If the function expressing the correlation in height between any two points on the surface is expressed as a power law in the inverse of the distance between the two points the exponent is found (34) to vary with temperature for the Ni(115) surface as indicated in Figure (5); the abrupt increase in the roughness exponent, \( \chi_q \), at \( \sim 450K \) is interpreted as indicating the onset of roughness. It is not entirely clear, however, that the observed scattering effects are in fact due to spontaneous kink formation. An experiment combining the diffraction method with STM observations of the configuration of step edges would be extremely interesting.
(iii) Atomic Step Clustering and Facetting

Surfaces vicinal to low index planes of close-packed crystals are made up of arrays of atomic steps and terraces. Such surfaces give rise to characteristic splitting of LEED beams \(^{(35,36,37)}\), (as illustrated in figure (6) \(^{(38)}\)), with the magnitude of the difference in scattering vector between the beams reflecting the peak in the distribution of terrace dimensions. Individual steps on such a surface will meander in two dimensions so that neighboring steps will have points of close approach. If the mean interaction between steps is attractive there will be a tendency toward low temperature clustering whereas at sufficiently high temperature a single step array (of higher configurational entropy) will be favored. Figure (7) \(^{(39)}\) shows the average terrace width as a function of temperature deduced from diffraction patterns of the type shown in (6a) and (6b). The observed hysteresis associated with temperature cycling could be indicative of a first order transition involving 2-phase coexistence or may reflect kinetic limitations. Careful measurements of the profiles of the scattered beams are currently being made to decide between these two possibilities.
Facetting may be viewed as an extreme case of step rearrangement in which an initially flat surface undergoes a morphological transition to one composed of extensive regions of two or more surface orientations. Most transitions of this type for metal surfaces seem to be associated with the presence of an adsorbed layer but the surface tension of some ionic and covalent crystals is sufficiently anisotropic that facetting occurs on clean surfaces of these materials. An interesting example is the facetting of Si surfaces near (210) to (211) surfaces in other zones.

IV. Phase Transitions involving Adsorbed Layers

(i) Open Adsorbed Systems

Adsorbed layers in equilibrium with a vapor phase, where coverage is determined by temperature and gas pressure, have been studied most extensively for gas molecules which bond weakly through van der Waals potentials to the substrate. Rare gases on the graphite basal plane have been widely studied by structural and thermal techniques. For these systems the heat of adsorption is sufficiently small that low coverages can be obtained in the easily accessible gas pressure range; with strongly chemisorbed molecules (heats of adsorption \(\gtrsim 2\text{eV}\)) extremely small effective gas pressures are required for equilibrium coverages significantly below a monolayer.

Figure (8) shows a set of adsorption isotherms for Xe on graphite; the abrupt increase in coverage from a low value to that of a dense ordered overlayer is characteristic of the formation of a dense phase of attracting molecules through a first order transition. Measurements on the segregation of carbon to Ni(III) surfaces from a dilute solid solution show qualitatively similar behavior (Figure (9)). The abrupt increases in carbon coverage to form a
monolayer graphite phase can be measured as a function of bulk carbon concentration and used to establish the diagram of figure (10) (8).

Figure (11) shows a pressure vs. 1/T phase diagram for CO adsorbed on Pd(100) (7). For this system the heat of adsorption is sufficiently low (<1.5eV).
that equilibrium coverages well below one monolayer can be achieved. The slope of the 2-phase coexistence lines should be described by equation (2).

(ii) Closed One-component Adsorbed Systems

The vast majority of the work on surface phases on crystal surfaces has involved adsorbed layers which are not in equilibrium either with the vapor or solid solution. The average coverage remains fixed as temperature is varied up to some value where diffusion or desorption rates become appreciable. Significant portions of \( \varepsilon \) vs \( T \) phase diagrams have been mapped out for several chemisorption systems. The case of \( \text{O} \) on Ni(111) is among the most studied and best understood systems at present. The phase diagram \((11,45)\) of this system is shown in Figure (12). One of the most interesting features of the diagram is the existence of a well ordered p(2x2) phase which disorders, at constant \( \varepsilon \) (\( \sim 0.25 \)) to a (1x1) phase at a temperature of \( \sim 450^\circ\text{C} \). This phase and its disordering were in fact noted by Davisson and Germer \((46)\) in their historic study of electron diffraction from a (111) Ni surface. A similar transition seems to occur \((47)\) for S on Ni(111). Park and coworkers \((45)\) have made a careful study of the profiles of individual superlattice diffraction beams from O on Ni(111) as a function of temperature in order to extract critical exponents for this continuous order-disorder transition.

(iii) Closed Two-Component Adsorbed Systems

The study of binary adsorbed layers is still at an early stage and only a very few results have been reported. Such quasi 2-dimensional alloy systems are likely to prove extremely interesting and would be expected to exhibit all of the features (- miscibility gaps, eutectics, eutectoids, compound formation, etc.) found for 3-dimensional alloys. It is also likely that the phase diagrams for binary adsorbed layers will be of great value in understanding surface
reactions. Figure (13) (12) is a phase diagram for the CO-Ar model system. Figure 13. Phase diagram (12) for the binary adsorbed layer, CO + Ar, on graphite. CD is a commensurate disordered phase, IC an incommensurate phase, HB an orientational ordered phase and PW a compositionally ordered phase.

physisorbed on graphite. The phase boundaries were established from measurements of the temperature variation of the intensities of electron and neutron diffraction beams. The various phases involve orientational ordering of the CO molecular axis as well as its location relative to the underlying substrate atoms. As can be seen there are indications of several critical points at which 3 phases coexist in equilibrium.

Figure (14) (48,49) shows some preliminary observations on the strongly adsorbed O and S on a Ni-Fe(100) surface.
chemisorbed S+O overlayer on an alloy substrate. The LEED studies in this case indicate a miscibility gap in which a S rich C(2x2) phase coexists with an O rich C(2x2). Whether the gap terminates with a critical point or a eutectoid is not well established at this time. This is a particularly interesting type of diagram in connection with the effect of S on the reaction of transition metals with oxygen.

References

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C. Briant: What are the sizes of the oxygen C(2x2) and sulfur C(2x2) regions in the two phase regions?

J.M. Blakely: We have no direct evidence yet on this question. However, they seem to be at least comparable to the coherence of the LEED beam, i.e. 150Å.

J. Narayan: Could you comment on relative abundance of simple and double steps on Si(100) surfaces. Is there any work on temperature dependence? Thermodynamically, it would seem double steps should be favored over single steps.

J.M. Blakely: The occurrence of single or double steps seems to depend on the axis about which the surface is tilted. There is evidence that surfaces lifted toward (111) have biatomic steps.

V. Pontikis: The results obtained by helium beam diffraction on Cu(115) (Lapujoulade et al) have shown that interaction energies, $W_u$, between steps are quite small: $W_u < 120K$. Dislocations in grain boundaries interact usually elastically and the interaction energies per atom can be much higher than those between steps. How is it possible to expect a roughening of grain boundaries by analogy with what happens to free surfaces?