1 Surface Alloys

1.1 Introduction

1.1.1 Surface Alloys and their Role in Surface Science

A surface alloy is a mixture of metals on a homogeneous substrate, typically an atomically flat surface of a monometallic single crystal. One or more guest metals are deposited onto this crystal and blended with each other or with the host metal. This is often intentionally promoted by thermal annealing. By definition, a surface alloy is confined to a few atomic layers, and from a surface science perspective the relevant properties can usually be broken down to features of the first 1 to 3 layers.

Whereas many surface alloys were initially encountered as (unintended) side effects of metal heteroepitaxy [1], they have nowadays become a valuable category of model surfaces. Due to their fast and flexible preparation as compared to bulk alloys they are often used to specifically study selected electronic, magnetic, or chemical [2][3] surface properties resulting from metal-metal intermixing.

Thermodynamically, however, steep concentration profiles as they are typical for surface alloys are inherently metastable. If nothing else, it would eventually be the entropy gain to drive a homogeneous dissolution of the guest metal(s) into the host bulk. Surface alloy preparation thus requires temperatures where near surface intermixing is faster by orders of magnitude than dissolution into the bulk, thus establishing local equilibrium [4, 5].
After a brief definition of the three most important types of surface and near-surface alloys, this chapter will illustrate the phenomenon of surface alloying by a number of representative examples. A focus will be on the behavior at the temperatures where the near-surface intermixing takes place, describing also the atomic scale place exchange processes as far as they are known today. Special emphasis is put on the “survival instinct” of many surface alloys, i.e., their driving force to remain at the surface even at elevated temperatures and their stability even against attempts to deliberately bury them under fresh layers of the host metal. It is interesting to look at the underlying thermodynamic driving forces and how they can be predicted on the one hand and how these initially rather abstract driving forces make their way down to the atomic scale processes on the other.

The last section will concentrate on the lateral distribution of the respective metals in a surface alloy. We will exemplarily show how the atom distribution in a disordered surface alloy can be quantitatively characterized based on STM data, and how such a distribution can be predicted by Monte-Carlo (MC) simulations. This will include the description of a simplified pairwise interaction model and how the energy parameters for such a model can be derived from experiments on the one hand and from ab-initio calculations on the other. We will show that even a very basic energy model is capable of accurately predicting the atom distribution in a surface alloy via MC simulations. MC simulations also allow predicting the (hypothetic) surface structure at temperatures where sluggish kinetics suppresses re-organization of the atoms in an experiment. A key parameter to be derived from such simulations is the temperature of the order-disorder transition of the respective system.

Most topics in this chapter will be illustrated by examples from related scanning tunneling microscopy (STM) studies. STM with chemical contrast [9–15] provides comprehensive pictures of the composition of the surface layer and the lateral distribution of its constituents. STM provides quantitative information about the atom distribution even in the absence of periodic long-range order, i.e.,
when diffraction techniques become less accurate. Such data provide a deeper understanding of the low
dimensional metallurgic effects that determine the formed structures and allow studying structure-
property relationships in various types of model studies.

### 1.1.2 Classification of Surface Alloys

The easiest case of a truly two-dimensional alloy is a ternary system of the type (A+B)/C, where the
host metal C has a significantly higher melting point than the deposited guest components A and B. This
ensures that A and B can be intermixed at a temperature where tracer diffusion of metal A or B into the
bulk of C is still negligibly slow. Surface alloys of this kind will be referred to as "Type III". Their
fabrication is schematically illustrated in Figure 1.1.1 e-f. A less straightforward way of fabricating a
surface alloy is by depositing only one foreign metal and forming a mixture of this guest metal with host
metal atoms (Figure 1.1.1 a-d). Since this involves place exchanges between host and guest atoms, the
guest atoms can in principle become incorporated into the substrate. It then depends on the
thermodynamic properties of the respective metal combination whether a surface alloy (Type I, Figure
1.1.1 d) or rather a sub-surface alloy (Type II, Figure 1.1.1 e) is formed.

![Figure 1.1.1](image)

**Figure 1.1.1** Fabrication of three types of surface alloys; upper/lower row = before/after annealing. (a,b) Type I surface alloy: one guest metal A alloys into outermost layer of host B upon annealing; (c,d) Type II (sub-)surface alloy: one guest metal B alloys into subsurface layer of host A upon annealing; (e,f) Type III surface alloy: guest metals A and B are intermixed on a higher melting host metal C.
As will be explained in more detail later in this chapter, exchanging the host and guest roles of a given couple of metals A and B will in most cases go along with a swap from a Type I to a Type II surface alloy and vice versa.

1.2 The Effect of Annealing – Case Studies and Predictability

1.2.1 Type I: (A+B) / B Surface Alloys

In Type I surface alloys, host atoms are replaced by guest atoms, hence a temperature is needed where host atoms leave their places, create vacancies, or exchange with guest atoms. As explained in some detail in Chapter 8.1 of Volume 2 of this book, the onset temperatures of the distinct thermally induced phenomena are best understood on a generic scale relative to the bulk melting temperature $T_m$ of the respective metal (Figure 8.1.1 in Chapter V of Volume 2). In Type I surface alloys the respective parameters for the host metal are decisive. Rather open surfaces such as Cu(110) [16] or Cu(100) [17–23] exhibit a considerable concentration of mobile vacancies even at room temperature (for a comprehensive overview of Cu(100) supported surface alloys see ref. [24]). Consequently, deposition of foreign metals onto such surfaces goes along with surface alloying even at ambient or cryogenic temperatures [1]. Figure 1.2.1 exemplarily shows an STM image and a structure model of the c(4x4) structure formed upon deposition of 3/8 ML of Pb onto Cu(100) at 300 K [22, 23].
Figure 1.2.1 Ordered Type I surface alloy formed upon vapour deposition of 3/8 ML Pb on Cu(100) at 300 K. (a) STM image of the labyrinth-like pattern formed by rotational domains of the c(4x4) surface alloy [22, 23]. (b) Structure model of a single domain of the c(4x4) surface alloy [23]. From Refs. [22, 23].

A high concentration and mobility of vacancies in the Cu(001) surface at room temperature was confirmed in time resolved STM studies. Surface alloys involving small amounts of In [19][20] or Co [21] allow to make use of the guest metal atoms as tracers. Quantitative evaluation of the frequencies of their various short and long-distance jumps confirmed vacancy diffusion as lateral transport mechanism (see Figure 1.2.2) [19–21].

The presence and mobility of vacancies has a twofold effect on the formation of surface alloys. First, the vacancies can trap deposited foreign metal atoms shortly after their landing on the surface, thus
incorporating them into the surface atom layer. Second, they ensure lateral transport within the intermixed layer, enabling thermodynamic equilibration of the atom distribution. This is how ordered patterns like the one in Figure 1.2.1 can be formed even at room temperature.

On more densely packed surfaces such like the (111) face of fcc crystals the mechanism of surface alloying at lower temperatures, if observed at all, is a different one. Surfaces of lower melting metals such as Cu(111) or Ag(111) exhibit dynamic step fluctuations at room temperature [25]. Guest metal adatoms that diffuse to the step edges will thus have a certain probability to become surrounded by host metal atoms and thus to become incorporated into the upper terraces. Figure 1.2.3a illustrates such a case for Pd atoms getting incorporated into an ascending step on Cu(111). The bright “spikes” near the step are due to the fluctuations. Apart from these fluctuations, however, there is no evidence for diffusion of Pd into the Cu(111) terraces. This indicates a low concentration of vacancies in the Cu(111) surface.

On Ag(111), an intensively studied surface alloy is of Sb$_x$Ag$_{1-x}$/Ag(111), which was discovered indirectly: the homoepitaxial growth on Ag(111) (see Chapter 1 in this volume) turns into a layer-by-layer mode even at 300 K or below if the surface is covered by about 0.2 ML of Sb, and Sb was found to remain floating in the outermost surface layer [27–30]. Closer investigations gave evidence for Sb to be sited in substitution sites (cf. Figure 1.1.1b)[31]. As will be discussed in some detail further below, the phenomenon of floating guest metal content in the surface layer is closely entangled with Type I surface alloys.
Figure 1.2.3 STM image of two Cu(111) terraces that are separated by a monoatomic step. Bright spots appear near the step edges upon vapour deposition of a small amount of Pd. These spots are Pd atoms at substitution sites that were incorporated into the upper terrace by step fluctuations. From Ref. [26].
Homogeneous surface alloys on densely packed surfaces such as the (111) or (0001) surfaces of fcc or hcp metals, respectively, usually require higher temperatures to ensure homogeneous surface intermixing. This will be illustrated for the well-studied system Pt$_x$Ru$_{1-x}$/Ru(0001) in the following.

Figure 1.2.4 shows STM images of a Ru(0001) surface that was modified by 0.4 ML Pt and subsequently annealed at 850 K or 900 K. Atomically resolved images reveal an onset of surface alloying, which manifests itself in a locally “rough” appearance of the Pt islands and step decorations and also of the Ru atoms.
terrace areas surrounding them. Closer inspection reveals that first Ru substrate atoms are replaced by Pt and are then incorporated into Pt islands and ribbons [32].

More homogeneous Pt$_x$Ru$_{1-x}$/Ru(0001) surface alloys can be achieved by the same procedure, but applying higher annealing temperatures. This is demonstrated in Figure 1.2.5, where the triangular monolayer islands obtained by vapor deposition of 0.5 ML Pt at 300 K are transformed into a flat and homogeneous Pt$_{0.5}$Ru$_{0.5}$/Ru(0001) surface alloy by annealing at 1350 K [33, 34, 8, 35]. The identification and characterization of Type I surface alloys like this by STM is straightforward: the two types of atoms clearly differ in their apparent height, and the amount of dark atoms matches the amount of Pt deposited initially. Hence, both the conservation of Pt in the outermost layer and its lateral distribution can be confirmed and quantified, respectively, by STM. Thorough statistical analysis of many Pt$_x$Ru$_{1-x}$/Ru(0001) surface alloys revealed that the atom distribution is very close to a random one (see section 1.3.4) [8].

![Figure 1.2.5](image_url) Fabrication of a type II surface alloy [8]: (a) 0.5 ML Pt deposited onto Ru(0001) at 300 K. (b) The same surface after annealing to 1350 K. Atomically resolved images (c) on a large terrace and (d) of an island edge (see frames marked in (b)) showing a Pt$_{0.5}$Ru$_{0.5}$/Ru(0001) surface alloy with identical composition on islands and surrounding terraces. Pt atoms appear darker than Ru atoms in the atomically resolved images. From Ref. [8].
Figure 1.2.6 Pt content counted in Pt$_x$Ru$_{1-x}$/Ru(0001) surface alloys as a function of initial Pt coverage. Dotted line: no Pt loss; dashed/solid line: quasi-equilibrium of the Pt contents in the two outermost layers as calculated from calculated segregation energies (see ref. [8] for details).

The lateral distribution in surface alloys will be discussed in section 1.3. At this point, we wish to draw the attention to the conservation of the Pt surface content during the annealing step. Figure 1.2.6 quantitatively illustrates this behaviour for Pt$_x$Ru$_{1-x}$/Ru(0001), comparing the amount of Pt atoms counted in atomic resolution images (e.g., Figure 1.2.5 c-d) to the Pt coverage as apparent from the initial island morphology (e.g., Figure 1.2.5). The same behaviour can also be observed by Auger Electron Spectroscopy, which shows identical spectra before and after the annealing step forming a Type I surface alloy (see, e.g., Figure 1.2.10). As discussed in more detail in ref. [8], measurable losses of Pt after annealing are only observed for Pt coverages of 0.8 ML and above (see Figure 1.2.6). These can be attributed to “thermal excitation”, i.e., Ru atoms that diffuse to the surface during the annealing step and are frozen there once the temperature drops again.
A second important observation is the island morphology that Figure 1.2.5 shows for the surface before and after annealing. The round monolayer islands of the alloyed surface have the same Pt content as the surrounding terraces (see the STM image in Figure 1.2.7 for illustration). This is only possible if essentially no Pt is buried under the islands. The surface alloy formation can thus be summarized as follows: host and guest atoms effectively intermix and homogenize the surface stoichiometry by effective lateral diffusion. As a boundary condition, all guest atoms remain in the outermost layer. In the picture of atomic scale processes, this can be rationalized as follows: during the annealing step, islands and step edges transform into a 2D adatom gas (Figure 1.2.8 a-ii). The adatoms exchange places with underlying surface atoms (Figure 1.2.8 a-iii). Initially, the adatoms and surface atoms will be mainly guest (A) and host (B) species, respectively. Then the adatoms and surface atoms
will enrich in B and A, respectively. Both species will quickly diffuse on the surface and thus contribute to a re-arrangement of surface steps and islands (Figure 1.2.8 a-iv). The key for the observed conservation of the guest (A) metal content in Type I surface alloys now lies in the manner how islands and steps grow, move, and shrink. If this would happen without preferences, increasing amounts of A would become buried and would no longer exchange with adatoms. As will be discussed in detail more below, however, Type I surface alloys with a conservation of A in the outermost layer will typically be those where A has negative surface segregation energy in the guest B [4, 36, 5]. This implies that thermodynamically an exposed A atom is energetically favoured over a buried one. But why should this keep a diffusing adatom from attaching to an island that would then bury an underlying A atom (Figure 1.2.8 b-i)? This can be understood in a pairwise interaction model. If A and B atoms are bound more strongly to B then to A, then both will remain longer at sites where they interact with as many B atoms as possible. Hence, islands and steps will preferentially overgrow B atoms (Figure 1.2.8 b-ii) whereas A atoms will be exposed much longer. This implies a high probability to be re-exchanged against a B atom (Figure 1.2.8 b-iii). Hence, the island and morphology in a type II surface alloy can change whilst keeping the A atoms exposed (Figure 1.2.8 b-iv).
The island morphology itself will be driven towards a minimization of low-coordinated edge atoms, i.e., larger islands (eventually vanishing by coalescence). Since embedded guest metal atoms next to an island will block any further extension of the latter until they get replaced by host metal ones, however, island coarsening of Type I surface alloys becomes much slower as compared to “normal” Ostwald ripening in metal epitaxy (see Figures 20 and 21 in Chapter “Epitaxial Growth of Thin Films” by Harald Brune). The surface alloying mechanism described above is nicely illustrated in two Low Energy Electron Microscopy (LEEM) studies. These demonstrate and explain the migration of Sn islands during the formation of a bronze monolayer (Cu-Sn) on Cu(111) (see Figure 1.2.9) [37] and a labyrinthine Pd island growth during the formation of a Pd,Ru$_{1-x}$ surface alloy on Ru(0001) [7].
In summary, Type I surface alloys on more densely packed surfaces can be formed at temperatures where “horizontal” adatom diffusion and “vertical” exchange between adatoms and surface atoms are sufficiently fast. Vacancy diffusion in the alloyed layer may contribute to the intermixing, but once “vertical” exchange processes are activated, adatom diffusion will be sufficiently fast anyway and will thus dominate the lateral transport. In combination with the preferred attachment sites for diffusing adatoms, the processes of adatom diffusion and exchange are sufficient to understand how a reorganization and local thermodynamic equilibration of the two outermost surface layers can occur. The restriction to these layers can be rationalized by the fact that the energetically most expensive transition states of the transport processes only involve a lowered coordination of surface atoms. Bulk diffusion processes, on the other hand, can be expected to exhibit much higher kinetic barriers, thus setting in only at higher temperatures. This defines the upper limit of the temperature window where well-defined and uniform type II surface alloys can be formed.
1.2.2 Floating of Guest Atoms in Type I Surface Alloys

The interplay between metal-metal interactions, adatom diffusion and exchange processes described in the previous section should also lead to a re-exposition of foreign metal atoms that have been deliberately overgrown by islands of the host (or substrate) metal. For the systems Pt,Ru$_{1-x}$/Ru(0001) and Pd,Ru$_{1-x}$/Ru(0001), this could indeed be experimentally confirmed [35].
Figure 1.2.10 shows a sequence of preparation steps that confirm that the guest (Pd) atoms in a Pd,Ru_{1-x}/Ru(0001) surface alloy can “dig” themselves out again if they get buried under a layer of host (Ru) atoms vapor deposited on top of the alloy. The Auger Electron Spectra on the right hand side of this figure give direct quantitative evidence for this behaviour: the first two spectra are essentially identical and thus confirm that the Pd:Ru ratio in the outermost layer is the same before (a) and after (b) the transformation of the Pd islands into a Type I surface alloy. The second pair of spectra shows that the Pd signal decreases by about 50% when the surface alloy (b) is overgrown by 1.2 ML of vapor deposited Ru (c). After re-annealing to 1150 K, the resulting spectrum (d) is again identical to that of the initial Pd island covered surface (a).
Figure 1.2.10 Floating of a Pd$_{0.44}$Ru$_{0.56}$/Ru(0001) surface alloy observed by Auger Electron Spectroscopy. Spectra obtained after each of the four stages of surface modification are compared pairwise. The grey lines are thicker to make the black lines visible in the pairwise comparisons. Stages: (a) 0.44 ML Pd on Ru(0001) (see Figure 1.2.11 a); (b) after annealing at 1150 K (see Figure 1.2.11 b,c); (c) after overgrowth by 1.2 ML Ru (see Figure 1.2.11 d); (d) after annealing to 1150 K (see Figure 1.2.11 e,f). From Ref. [38].
Figure 1.2.11 Floating of a Pd$_{0.44}$Ru$_{0.56}$/Ru(0001) surface alloy observed by STM. (a) 0.44 ML Pd deposited on Ru(0001) at 300K. (b) surface morphology and (c) atomic scale structure after annealing to 1150 K for 10 s. (dark/bright atoms = Pd/Ru). (d) Surface morphology after overgrowth of the surface alloy by 1.2 ML Ru at 500K. (e) Surface morphology and (f) atomic scale structure after annealing to 1150 K. (morphology images: 200 x 200 nm$^2$; atomically resolved images: 6 x 9 nm$^2$). From Ref. [35].

STM images tracking the same sequence of surface modifications are shown in Figure 1.2.11. The atomic scale surface alloy of the initial (c) and the re-floated Pd$_{44}$Ru$_{56}$/Ru(0001) surface alloy (f) are indeed indistinguishable. Examples like this strongly emphasize the statement that Type I surface alloys not only reflect an interrupted dissolution of a metallic adlayer via bulk diffusion but that they indeed reflect a local equilibrium state that is stable against perturbations.
1.2.3 Type II: $A/(A+B)/A$ (Sub-)Surface Alloys

If a system $(A+B)/B$ is forming Type I surface alloys, then the exchange of $A$ and $B$ will in the majority of the cases lead to a system forming Type II (sub-)surface alloys (see following section). A typical example is the system $\text{Ru}/\text{Pt}(111)$ [39, 40], i.e., the counterpart of the stable surface alloy $\text{Pt}_x\text{Ru}_{1-x}/\text{Ru}(0001)$ (Figure 1.2.5, Figure 1.2.7). As illustrated in Figure 1.2.12, Ru deposited at Pt(111) forms islands that turn into bilayer islands at slightly elevated growth temperatures. Bilayer islands are formed because (i) Ru binds more strongly to Ru than to Pt, and (ii) a Ru monolayer is more reactive than a Ru bilayer [40]. For $T > 573$ K, the bilayer morphology is replaced by one dominated by monolayer islands, which vanish at $T > 773$ K. As illustrated by the drawings in Figure 1.2.12 e – h, the collapse of the bilayer morphology goes along with the onset of surface alloying. Auger electron spectroscopy data confirm that the outermost layer of these surface alloys is enriched in Pt, and that the near-surface region remains enriched in Ru up to at least 773 K [39].
Hence, for both systems Ru/Pt(111) and Pt/Ru(0001) there is a temperature window for effective exchange between adatoms and surface atoms and adatom diffusion (see Figure 1.2.8) and both systems form an alloyed thin film. Due to the lower surface energy of Pt as compared to Ru, however, this film is exposed on the Ru(0001) surface but capped by a Pt-rich layer on Pt(111) [39].
A quite fascinating sub-surface alloy is the system Ir / Cu(100). Upon vapor deposition of 0.6 ML Ir on Cu (001) at 620 K, subsequent STM imaging shows ordered patterns such as the one visible in Figure 1.2.13 a. Ion scattering experiments, on the other hand, revealed a negligible Ir content of the outermost layer. The pattern thus belongs to rotational domains of an ordered Cu-Ir structure covered by a monolayer of Cu (Figure 1.2.13 b,c) [41]. Similar sub-surface alloys (yet not always ordered) are also observed on Cu(100) for other guest metals with slightly higher atomic radii and higher surface energy [42] as compared to Cu (e.g., Pd, Pt, Rh) [24].

In the context of (electro-)chemical model studies, Pt(111) surfaces modified by sub-surface 3d transition metals are a well-studied class of Type II (sub-)surface alloys. These are of particular interest because of their tuning effect on the chemical and (electro-)catalytic properties of Pt(111) [43]. Among those, Ni/Pt(111) has become a prototype system for sub-surface alloying. The reader is referred to Ref. [44] for an illustrative and detailed overview. An important observation common for Type II surface alloys is the low onset temperature of near-surface intermixing, i.e., of the observable disappearance of guest species from the outermost layer. According to Ion Scattering Spectroscopy data, increasing/decreasing peaks of the host/guest metal are observable just above room temperature for Ni/Pt(111) [45].
Figure 1.2.14 Onset of surface alloying at room temperature observed by STM: Au(111) after deposition of a small amount of Pt at room temperature. Pt spontaneously alloys into the outermost layer and occupies substitutional sites. From Ref. [46].

Figure 1.2.14 illustrates that for the model system Pt/Au(111), a spontaneous incorporation of Pt atoms into the Au(111) surface can indeed be directly observed already at room temperature [46]. As will be discussed in more detail in the following section, the size ratio between host and guest metal plays a key role in this context: it is intuitive that smaller guest atoms encounter smaller barriers to penetrate the host surface. An observable “stopover” in the outermost layer is thus not surprising, even if thermally promoted diffusion will eventually transfer them into the sub-surface layer as their local-equilibrium site. Figure 1.2.15 shows exemplarily shows XPS and STM data for Cu/Pd(111) as a typical case. Cu films of 0.5 ML, 1.1 ML, and 2 ML initial thickness are heated to increasing temperatures in steps of 50 K and show a continuous decrease in the detectable (near-)surface Cu content. Atomically resolved STM images as the one in the inset in Figure 1.2.15 b show a versatility of apparent atom heights, in contrast to the clear distinguishability of atom types seen for other systems shown in this chapter. Hence, Cu/Pd(111) may not even locally equilibrate into a sub-surface alloy but rather build up a Cu concentration profile that ranges further into the bulk [47].
1.2.4 Surface or sub-surface alloying?

Most of the systems discussed in the preceding sections were prepared by annealing to temperatures where near-surface intermixing is possible but bulk diffusion is still negligible. Near-surface intermixing takes place via adatom diffusion, vacancy diffusion, filling of vacancies with adatoms, and exchange between adatoms and underlying surface atoms (cf. Figure 1.2.8). The intermixing processes are thus restricted to adatoms and the underlying surface layer. In cases where the atomic radius of the guest metal is larger than that of the host metal, there is a very obvious reason why guest metal atoms are incorporated into the host surface layer rather than remaining in adlayer islands (Figure 1.1.1 a-d). Due to the reduced coordination of surface atoms, (non-reconstructed) metal surfaces are under tensile stress. The reduction of this tensile stress by the partial replacement of host atoms by larger guest atoms provides a simple driving force for the formation of Type I surface alloys [49, 50]. At the same time, larger atoms will also encounter an intrinsically higher barrier that prevents them from diffusing further into the bulk. This barrier can also be a thermodynamic one because many type II surface alloys involving larger guest atoms are formed by bulk immiscible systems.
Pd$_{0.52}$Ru$_{0.48}$/Ru(0001), Ag$_{0.46}$Pt$_{0.54}$/Pt(111), Au$_{0.44}$Pt$_{0.56}$/Pt(111), and Ag$_{0.49}$Pd$_{0.51}$/Pd(111) in Figure 1.2.16 are typical examples for this class of Type I surface alloys. It should be noted that this direction of size mismatch seems to be a prerequisite for the stabilization of Type I surface alloys, i.e., we are not aware of any documented Type I surface alloy where the guest atom has a smaller atomic radius than the host atom. Some experimentally observable systems where smaller guest atoms are blended into the outermost layer of the hosts are not stable against thermal annealing and/or overgrowth by the host metal (see, e.g., the example of Cu/Pd(111) in Figure 1.2.15). However, it is possible to have larger guest atoms whose high surface energy drives them into the sub-surface layer (e.g., Pd, Pt, Rh in Cu(100) [24]).

Considering only the two outermost layers as a bimetallic system in local equilibrium, the system can behave in three different ways. It can form (i) a Type I surface alloy (guest mainly exposed), (ii) a Type II (sub-) surface alloy (guest mainly buried), or (iii) two layers of similar composition. The decisive parameter is the surface segregation energy $E_{\text{seg}}$, which is the thermodynamic driving force to move a subsurface guest metal from the bulk to the surface of the host metal (see Chapter ... in Volume 3). In transition metal alloys $E_{\text{seg}}$ essentially depends on the difference in the surface energies [42] of host and guest metal and on their respective crystal structures [54]. For densely packed surfaces, Ruban et al.
have published a comprehensive table of segregation energy values calculated by DFT [4, 6]. Host-guest combinations with sufficiently negative surface segregation energy of the guest will form Type I surface alloys according to Figure 1.1.1 b, whereas a positive value will generate Type II (sub-)surface alloys similar to Figure 1.1.1 d. So far these ab-initio calculated trends were confirmed in countless surface microscopy and spectroscopy studies [8, 45, 51, 35, 52, 44, 55, 53]. Some illustrative examples are the systems shown in Figure 1.2.5, Figure 1.2.12, and Figure 1.2.16, whose Type II surface alloy behaviour was foreseen. Likewise, the instability of the guest species in Ru/Pt(111) (cf. Figure 1.2.12) [39], Cu/Pd(111) (cf. Figure 1.2.15) [47], or Ni/Pt(111) [45, 44] in the outermost layers of the respective host were correctly predicted.

**Figure 1.2.17** Examples of DFT based surface energy curves belonging to the four generic classes of surface alloys defined in Ref. [4]. The STM images are showing Ag$_{0.07}$Cu$_{0.93}$/Cu(100)[56] and Ag$_{0.46}$Pt$_{0.54}$/Pt(111) [57]. Plots reproduced from Ref. [4], STM image on the left from Ref. [56].

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In their work, Christensen et al. divided surface alloys into four generic classes [4], which are illustrated by four different surface composition dependent surface energies in Figure 1.2.17. In the used thermodynamic model, the foreign metal is assumed to be either in the outermost surface layer or dissolved in the bulk of the host metal. The upper row (a and b) includes all surface alloys where the surface energy becomes lower with increasing amounts of foreign metal in the surface. In the bottom row (c and d), the energy increases. Hence, only metal combinations described by one of the graphs in the upper row should form Type I surface alloys. Host-guest combinations that have ascending curves will either form Type II (sub-)surface alloys (if bulk diffusion is sufficiently hindered) or will not stabilize the guest species in the surface region at all.

The second structurally relevant aspect is the curvature of the curves. The straight lines in the diagrams reflect the energy for full phase separation, i.e., for surfaces that are partially covered by a closed monolayer of the host metal, but where the boundaries do not contribute to the energy. When the calculated curve is below the straight line, the respective metal combination will favor the formation of heterogeneous neighborhoods; otherwise it will rather tend to phase separation. At 0 K, the former systems would adopt ordered ground state structures, whereas the latter would prefer very large islands. As discussed above, thermal excitation counteracts the formation of ordered 2D alloys, and it also drives the phase separating systems into a higher dispersion than favorable at 0 K.

In the cited work, curves as in Figure 1.2.17 are listed for all combinations of transition and noble metals classes [4]. Specifically, the first and second derivative at $x_{\text{foreign}} = 0$ are tabulated. For all systems listed in this chapter as Type I surface alloys, the tabulated DFT data correctly predicted this behavior. Moreover, Ru$_x$Pt$_{1-x}$/Pt(111) is predicted to belong to class (c), which fits to the observed tendency towards the formation of a subsurface alloy overgrown by the host metal Pt (see Figure 1.2.12).
1.2.5 Type III: \((A+B) / C\) Surface Alloys

Starting point of a Type III surface alloy is a co-deposited binary metal film that is transformed into a surface alloy via thermal annealing. Figure 1.2.18 exemplarily illustrates this process for the system Cu + Pd /Ru(0001) in a series of STM images recorded along the preparation. Initially, 0.37 ML Pd are vapour deposited onto a clean Ru(0001) substrate kept at room temperature (1 ML = 1 monolayer = 1 foreign metal atom per substrate surface atom). The resulting island morphology is overgrown by 0.77 ML Cu. In STM images of the resulting surface (Figure 1.2.18 a), the Pd islands appear darker than the surrounding Cu areas. Moreover, second layer Cu atoms preferentially adsorb on the Pd areas. To achieve intermixing of the two guest metals, the sample was heated to a temperature that allows for sufficient movement of Cu and Pd but does not let them desorb into the gas phase or diffuse into the Ru crystal. For the present system, a suitable temperature window is \(700 \, \text{K} < T < 800 \, \text{K}\). As shown in Figure 1.2.18 b, annealing at 780 K for 30 s lets the second layer islands disappear and covers the Ru terraces by a virtually closed monolayer alloy. The dispersed distribution of Cu and Pd in this alloy is apparent from atomically resolved images as those in Figure 1.2.18 c and d, where Pd and Cu atoms appear bright and dark, respectively.
According to the STM data the Pd content in the outermost layer of this surface alloy is $x_{\text{Pd}} = 0.33$.

Since the overall amount of foreign metal exceeds 1 ML, there are some second layer step decorations which can be distinguished by their different apparent corrugation even in large scale images as in Figure 1.2.18 b. Images of this region such as in Figure 1.2.18 d (lower part) reveal a Pd content of only $x_{\text{Pd}} = 0.25$ on top of the local bilayer layer alloy. To guide the eye, the dashed lines in Figure 1.2.18 b and Figure 1.2.18 d mark a boundary between a first and a second layer alloy region. Such a depletion of Pd in bilayer regions can be rationalized by a stronger metal-metal bond of Pd to Ru as compared to Cu to Ru: keeping more Pd at the interface to the Ru substrate thus lowers the overall system energy [58].

Apart from the system for $\text{Cu}_x\text{Pd}_{1-x}/\text{Ru}(0001)$ [59–61, 58, 62], Ru(0001) substrates were also utilized to support 2D mixtures of Au + Pd [63, 11] (see Figure 1.2.19), Co + Ag [64, 65], Ag + Pd [61, 66], Ag + Au [67–74] and Ag + Cu [75–77]. It should be noted that the fact that Ruthenium is utilized so often as a substrate for type I surface alloys is mainly due to its high melting temperature and the well-established
methods of preparing clean Ru(0001) surfaces in the laboratory. Other high-melting metals such as Mo and W work similarly well as substrates.

![STM image of Pd$_{0.72}$Au$_{0.28}$/Ru(0001) as an example of a Type I surface alloy, prepared by co-deposition of Pd and Au onto Ru(0001) followed by annealing at 573 K. Bright / dark atoms = Pd / Au. From Ref. [11].](image)

**Figure 1.2.19**

1.3 *Lateral atom distribution in surface confined alloys*

The kinetic processes behind the formation of the different type of surface alloys are including effective lateral intermixing via adatom or vacancy diffusion. Hence, the lateral atom distribution of the surface alloys reflects a (local) equilibrium state. This section will give an overview about the physical and chemical information that can be determined from thorough analysis of such system specific atom distributions, and how these results can be related to predictions from theory.
1.3.1 Statistical short-range order analysis

Visual inspection of atomically resolved STM data as in Figure 1.2.5, Figure 1.2.7, Figure 1.2.11, Figure 1.2.16, and Figure 1.2.19 suggests that the atom distribution in surface alloys strongly depends on the metal combination. For instance, Cu$_{0.75}$Pd$_{0.25}$/Ru(0001) and Pt$_{0.75}$Ru$_{0.25}$/Ru(0001) are characterized by a large number of unlike neighborhoods [58, 62, 8], whereas equal neighborhoods appear to be favored for Pd$_{0.75}$Ru$_{0.25}$/Ru(0001) [51]. For direct comparison, three exemplary STM images are compiled in Figure 1.3.1. Despite the obvious preferences for homo- or heteroatomic neighborhoods, however, many surface alloys do not exhibit a long-range order but only a short-range order (SRO). As discussed more below, this is because the order-disorder transition temperature for many surface alloys is in a range where kinetic barriers for surface re-organization can no longer be overcome. Nevertheless, different systems can be quantitatively distinguished in their degree of SRO.

![Figure 1.3.1 Atom distribution in three different 2D alloys. (a) Pd$_{0.25}$Ru$_{0.75}$/Ru(0001) [51]; (b) Pt$_{0.25}$Ru$_{0.75}$/Ru(0001) [8]; (c) Cu$_{0.2}$Pd$_{0.8}$/Ru(0001) [58].](image)
For a quantitative description of the short-range order (SRO), it is common to calculate the so-called Warren-Cowley coefficients $\alpha(r)$ [78, 79, 11, 80]. The most intuitive definition of these parameters is

$$\alpha(r) = 1 - \frac{p_{AB}(r)}{x_B} \quad (1)$$

$p_{AB}(r) =$ probability to find an atom of type B in a distance $r$ to an atom of type A

$x_B =$ total fraction of type B surface atoms

For experimental data, it is common to evaluate $\alpha(r)$ for $r = 1, \sqrt{3}, 2, \sqrt{7},$ and 3, with $r$ given in units of the nearest-neighbor (NN) distance (see Figure 1.3.2). In a random distribution, where $p_{AB}(r) = x_B$, $\alpha(r)$ would be zero, whereas positive and negative values of $\alpha(r)$ reflect higher and lower numbers of like neighbors in a distance of $r$.

The simple formula mentioned above, however, is only applicable for data sets with periodic boundary conditions. For the evaluation of atom distributions measured by STM, where the atom matrices are naturally truncated at the boundaries, the evaluation should start with the pair correlation function $\langle p(r) \rangle$

$$\langle p(r) \rangle = \frac{\sum_{i,j} \delta_i \delta_j \delta_r (ij)}{\sum_{i,j} \delta_r (ij)} \quad (2)$$

$\delta_i = 1$ for atom type A; $\delta_i = -1$ for atom type B; $\delta_i = 0$ for an undefined atom

$i, j$: index of the lattice point

$\delta_r (ij) = 1$ when lattice points $i, j$ are separated by a distance $r$.
\( \delta_{ij}(r) = 0 \) in all other cases.

Based on \( \langle \pi(r) \rangle \) the SRO parameters are calculated according to [80] by

\[
\alpha(r) = \frac{\langle \pi(r) \rangle - (2x_B - 1)^2}{1 - (2x_B - 1)^2}
\]

Figure 1.3.3 shows atomically resolved STM images with chemical contrasts of type III surface alloys of the system Cu\(_x\)Pd\(_{1-x}\)/Ru(0001), whose fabrication was demonstrated in Figure 1.2.18. The images show no indication of long-range order (LRO) in the atom distribution. One might expect such a LRO for surface compositions close to those forming ordered bulk alloys [81], i.e., Cu:Pd=1:1 (Figure 1.3.3c) or Cu:Pd=3:1 (Figure 1.3.3e).

Despite the lack of LRO, however, the SRO of the atom distribution is significant for all surface alloy compositions shown in Figure 1.3.3. Figure 1.3.4 gives an overview of the SRO parameters \( \alpha(r) \) for a range of different Cu:Pd ratios, which was derived from a data set comprising more than 60,000 atoms.

For all compositions, the strongest deviation from random behaviour is observed for the nearest neighbourhoods. The negative value of \( \alpha(1) \) indicates a preference for unlike nearest neighbours over the entire range of film compositions investigated. This preference is partially reversed for a distance of 2 NN, where a small local maximum is visible for the surface with 25% Pd, indicating a preference for Pd atoms separated by 2 NN units, as they are present in the (2\times2) structure on the (111) plane of ordered Cu\(_3\)Pd bulk alloys. In a SRO analysis, such a (2\times2) structure would generate values of \( \alpha(2) = 1 \) and \( \alpha(r) = -1/3 \) for \( r \neq 2 \). In the STM based data, however, the variations of \( \alpha(r) \) are much less enhanced, and for \( r \geq 2 \), they lie within the margins of the statistical uncertainty. Even prolonged annealing at lower T was shown to not yield any periodic superstructure [60]. The following chapter will include a thermodynamic description of the lateral atom distribution, and it will show why ordered structures are experimentally inaccessible for most surface alloys.
Figure 1.3.3 STM images of various Cu$_x$Pd$_{1-x}$ / Ru(0001) Type I surface alloys. (a) Cu$_{98}$Pd$_{1}$, (b) Cu$_{91}$Pd$_{9}$, (c) Cu$_{79}$Pd$_{53}$, (d) Cu$_{68}$Pd$_{62}$, (e) Cu$_{78}$Pd$_{21}$, (f) Cu$_{89}$Pd$_{11}$. Cu atoms appear darker. (10 ×10 nm$^2$). From Ref. [58].
Figure 1.3.4 Comparison of Warren-Cowley SRO parameters determined from experimental data (o) and from MC simulations (×) at different compositions of the Cu$_x$Pd$_{100-x}$ layer. (a) Cu$_{09}$Pd$_{91}$, (b) Cu$_{21}$Pd$_{79}$, (c) Cu$_{47}$Pd$_{53}$, (d) Cu$_{68}$Pd$_{32}$, (e) Cu$_{70}$Pd$_{30}$, (f) Cu$_{89}$Pd$_{11}$. Exemplary STM-images: see Figure 1.3.3. From Ref. [62].

1.3.2 Additive Energy Model for 2D alloys

Ab-initio calculations for bimetallic systems via electronic structure theories, which allow descriptions by the rule of quantum mechanics, are either restricted to small clusters or to periodically ordered systems (see Chapter ... Volume 3) [80]. Calculations for small clusters, however, are of little relevance for the behaviour of extended surfaces. On the other hand, not all alloys possess a periodically ordered distribution of the components, as seen above. Instead, thermal excitation leads to a certain
degree of disorder in the atom distribution. The atom distribution can be simulated by Monte-Carlo (MC) techniques, which requires simplified, usually additive energy models [82–84]. Such models shall allow fast energy calculations for any possible configurations of the respective system.

Similar to the approach of cluster expansion for the description of three-dimensional structures [80] (see also Chapter ... in Volume 3), the total energy of a given distribution can be expressed via an Ising-like 2D lattice gas Hamiltonian of the form [85, 80]

\[
H\left(\{\vec{R}_i\},\{s_i\}\right) = V_0 + \sum_{\vec{R}_i} V_1(\vec{R}_i)s_i + \frac{1}{2} \sum_{\vec{R}_i} \sum_{\vec{R}_j} V_2(\vec{R}_i,\vec{R}_j)s_is_j + \frac{1}{6} \sum_{\vec{R}_i} \sum_{\vec{R}_j} \sum_{\vec{R}_k} V_3(\vec{R}_i,\vec{R}_j,\vec{R}_k)s_is_js_k + \ldots, \quad (4)
\]

where \(\{\vec{R}_i\}\) = 2D lattice including all sites occupied by the 2D alloy

\(\vec{R}_i\) = point \(i\) in the 2D lattice

\(\{s_i\}\) = occupation numbers

\(s_i, s_j, s_k\) = occupation numbers of sites \(i, j, k\)

\(s_i = -1 / +1\) for atom of type A / B at site \(i\)

\(H\left(\{\vec{R}_i\},\{s_i\}\right)\) = potential energy of a given occupation of the lattice points \(\{\vec{R}_i\}\) according to \(\{s_i\}\)

\(V_0\) = constant

\(V_1(\vec{R}_i)\) = site dependent energy contribution
\[ V_2(\vec{R}_i, \vec{R}_j) = \text{contribution from pairwise interactions; value depends only on distance between site } i \text{ and site } j. \]

\[ V_3(\vec{R}_i, \vec{R}_j, \vec{R}_k) = \text{contribution from triple interactions; value depends on geometric constellation of sites } i,j,k. \]

It is obvious that the terms \( s_i, s_i s_j, \) and \( s_i s_j s_k \) can only yield the values +1 or -1, depending on the occupation numbers, which thus determines for each site, pair, or triplet, whether \( V_i(\vec{R}_i), V_2(\vec{R}_i, \vec{R}_j), \) and \( V_3(\vec{R}_i, \vec{R}_j, \vec{R}_k) \) are added or subtracted from the overall energy. An ideal 2D alloy is supported on a homogeneous substrate, so that, apart from varying neighbourhoods, all surface atoms occupy equivalent sites. This means that \( V_i(\vec{R}_i) \) should be identical for all sites \( i, \) so that it includes the contribution of the surface composition to the overall energy \( H. \) For an energetic description of the SRO in the lateral atom distribution for a given surface composition, however, the contributions \( V_0 \) and \( V_1 \) can be skipped.

In the examples shown later in this chapter, the model will be further simplified by neglecting three-particle or higher interactions, which simplifies the 2D lattice gas Hamiltonian to

\[
H(\{\vec{R}_i\}, \{s_i\}) = \frac{1}{2} \sum_{\vec{R}_i} \sum_{\vec{R}_j} V_2(\vec{R}_i, \vec{R}_j) s_is_j = \frac{1}{2} \sum_{\vec{R}_i} \sum_{\vec{R}_j} V_{EPI}(r_{ij}) s_is_j
\]

(5)

The effective pair interaction (EPI) parameters \( V_{EPI}(r_{ij}) \) only depend on the distance \( r_{ij} \) between the sites \( i \) and \( j. \) For a 2D lattice occupied by either A (\( s=-1 \)) or B (\( s=+1 \)) atoms, these parameters are related to the interaction potentials \( V^{AA}(r), V^{BB}(r), \) and \( V^{AB}(r)= V^{BA}(r) \) via the equation [5]
\[ V_{\text{EPI}}(r) = \frac{V^{AA}(r) + V^{BB}(r)}{2} - V^{AB}(r) \]  \hspace{1cm} (6)

In a picture of pairwise attraction potentials, a coarse estimate for the attraction \( V^{AB}(r) \) between an A atom and a B atom at a distance \( r \) is about the average between the A-A attraction and the B-B attraction for that distance, i.e., \( V^{AB}(r) \approx \frac{1}{2} (V^{AA}(r) + V^{BB}(r)) \). One can easily test, however, that in such a simple case all lateral atom distributions would have the same energy. The EPI parameter \( V_{\text{EPI}}(r) \) is equal to the difference between the mean value \( \frac{1}{2} (V^{AA}(r) + V^{BB}(r)) \) and the actual pair interaction potential \( V^{AB}(r) \). Hence, it only accounts for that part of the interaction energies that affects the lateral distribution. A given EPI model for the atom distribution on a hexagonal lattice thus consists of a set of \( V_{\text{EPI}}(r) \) for \( r = 1, \sqrt{3}, 2, \sqrt{7}, 3, ..., r_{\text{max}} \), where \( r \) is given in multiples of nearest-neighbour (NN) distances.

Two common ways to determine the values \( V_{\text{EPI}}(r) \) are (i) fitting to the results of \textit{ab initio} data \cite{11, 80} (see also Chapter … in Volume 3\cite{11, 80}) or (ii) fitting to experimental results. Both will be briefly illustrated in sections 1.3.6 and 1.3.3 (following section) respectively.

\textbf{1.3.3 Energy Parameters Derived from STM Data}

Based on a given set of EPIs, a Metropolis Monte-Carlo (MC) algorithm \cite{86} can simulate lateral distributions for any temperature \( T \). The atomically resolved images of surface alloys are usually recorded at 300 K or below. At such low temperatures, however, place exchanges between surface alloy components are very slow for most systems, i.e., equilibration of the lateral atom distribution is kinetically hindered. The imaged atom distribution thus usually belongs to a temperature \( T_{\text{freeze}} \) ("freezing temperature") that the system went through during the cooling period of the annealing step.

To understand the influence of \( T_{\text{freeze}} \) on the simulated atom distribution, it is useful to recall the Metropolis MC algorithm: an \( m \times n \) matrix with a unit cell appropriate for the respective surface structure is filled with A and B atoms according to a given stoichiometry. In each MC step, two non-equal atoms are randomly selected, and based on the additive energy model the energy change \( \Delta E \)
associated with a swap of these two atoms is computed. If \( \Delta E \) is negative, the exchange is accepted. If \( \Delta E \) is positive, the exchange is accepted with a probability \( p = \exp(-\Delta E/(k_B T_{\text{freeze}})) \). This means, a random number in the range 0...1 is computed and the exchange is accepted if that random number is smaller than \( p \). The possible acceptance of energy increases can be referred to as “thermal excitation”. It introduces the configurational entropy into the simulated system, which would otherwise just converge into the minimum energy instead of the minimum free energy state. Many thousand swapping attempts and events are necessary to eventually drive the simulated towards a configurational equilibrium. Once that is reached, statistical data such as SRO parameters or the probability of certain atomic configurations can be extracted. Since the system is of finite size, those parameters will undergo statistical fluctuations, but the accuracy of the parameters increases with increasing number of iterations and samples. SRO parameters can thus be considered as “calculated” from EPI values.

For the inverse problem of calculating EPIs from measured SRO parameters, one has to repeat MC simulations whilst systematically varying a test set of EPIs. This can be done via a simplex downhill algorithm (or any other systematic search approach) [87, 88]. The inverse problem is considered solved once a set of EPIs yields SRO parameters that sufficiently agree with the experiment, e.g., by minimizing the function

\[
P_{\text{disagree}} = \sum_{r=1}^{N_{\text{max}}} \left( \alpha_{\text{exp}}(r) - \alpha_{\text{MC}}(r) \right)^2 , \quad (7)
\]

where \( \alpha_{\text{exp}}(r) \) and \( \alpha_{\text{MC}}(r) \) are the experimentally found and the simulated SRO parameter for distance \( r \), respectively.

Such a fit was applied for the Cu\(_x\)Pd\(_{1-x}\)/Ru(0001) system in Figure 1.3.3, yielding the simulated SRO parameters marked as crosses in Figure 1.3.4. The only instance where \( T_{\text{freeze}} \) appears in this procedure is the swapping probability into an energetically more positive configuration, \( p = \exp(-\Delta E/(k_B T_{\text{freeze}})) \). If
\( T_{\text{freeze}} \) is chosen wrong by a factor of, say, two, then all fitted energy parameters will be wrong by the same factor. In practice, however, \( T_{\text{freeze}} \) will be known with an accuracy of ± 10% or better.

### 1.3.4 Short-range order and Effective Pair Interactions – Experimental Results from Selected Model Systems

Different metal combinations are characterized by different “fingerprints” of the SRO and (fitted) EPI parameters. Figure 1.3.5 gives an overview about the atom distribution of five different Type I surface alloys, specifically, Au\(_x\)Pt\(_{1-x}\)/Pt(111) [52], Pd\(_x\)Ru\(_{1-x}\)/Ru(0001) [51], Ag\(_x\)Pt\(_{1-x}\)/Pt(111) [57], Pt\(_x\)Ru\(_{1-x}\)/Ru(0001) [8], and Ag\(_x\)Pd\(_{1-x}\)/Pd(111) [53], together with the respective SRO and EPI parameters for three different alloy compositions. Despite a direct analytic relation between the SRO coefficients and the EPIs was not yet found, one usually observes negative \( V(1) \) values for positive \( \alpha(1) \) and vice versa. The components Au\(_x\)Pt\(_{1-x}\)/Pt(111), Pd\(_x\)Ru\(_{1-x}\)/Ru(0001), and Ag\(_x\)Pt\(_{1-x}\)/Pt(111) tend to segregate into larger clusters, whereas the distribution in Pt\(_x\)Ru\(_{1-x}\)/Ru(0001) and Ag\(_x\)Pd\(_{1-x}\)/Pd(111) is rather disperse. The distribution in Pt\(_x\)Ru\(_{1-x}\)/Ru(0001) is so close to a random one (\( \alpha(r) \approx 0 \) for all \( r \)), that a simulation with all EPIs set to zero yields sufficient agreement with the experiment. In their tabulated surface alloy energy data, Christensen et al. have correctly predicted the clustered distribution of the first three metal combinations in Figure 1.3.5 and also the disperse distribution of Pt\(_x\)Ru\(_{1-x}\)/Ru(0001) [4]. For Ag\(_x\)Pd\(_{1-x}\)/Pd(111), however, the experiments revealed a small tendency towards segregation into larger clusters for small Ag contents but a preference for unlike neighbours at higher Ag contents (see SRO parameters in the lower right corner) [53]. Since the tabulated data only describe parabolic curves, however, such a changing trend was not possible to consider in the cited work [4].
Figure 1.3.5 Measured and simulated atom distribution in five different surface alloys. From left to right: Au$_x$Pt$_{1-x}$/Pt(111) [52], Pd$_x$Ru$_{1-x}$/Ru(0001) [51], Ag$_x$Pt$_{1-x}$/Pt(111) [57], Pt$_x$Ru$_{1-x}$/Ru(0001) [8], and Ag$_x$Pd$_{1-x}$/Pd(111) [53]. From top to bottom: atomically resolved STM images, EPI parameters derived from the experimental data, simulated atom distributions, measured (o) and simulated (x) SRO. From Ref. [38].
1.3.5 When Will a Surface Alloy Become Ordered?

As seen in many examples in this chapter, none of the surface alloys that require higher temperatures for their preparation exhibit a long-range order, even if ordered stoichiometric bulk phases exist for the respective metal combination. Intuitively, this is attributed to the low mobility at low temperatures, where the ordered ground states would be reached. Using the experimentally determined EPI parameters, it is possible to make a prediction for the temperature of the order-disorder transition of the respective system. This is done by a “simulated annealing” procedure, where MC simulations of the atom distribution are performed for continuously decreasing temperature. Figure 1.3.6 shows the result of a simulated annealing/cool-down procedure for a monolayer Cu$_2$Pd/Ru(0001) surface alloy, with EPI parameters fitted to the experimentally observed SRO [62]. Figure 1.3.6a shows a lateral atom distribution simulated for 600 K. Starting from 600 K, the simulation temperature was decreased in steps of 1 K, and for each temperature the MC simulations yielded an ensemble average for the mixing energy $\Delta H_{\text{mix}}$. $\Delta H_{\text{mix}}$ in Figure 1.3.6 becomes more negative with decreasing simulation temperature and reaches a base-line only at $T \approx 100$ K. The ground-state structure obtained for this simulation temperature is shown in Figure 1.3.6c. The simulated annealing thus shows that LRO in the system Cu$_x$Pd$_{1-x}$/Ru(0001) can only be expected for $T < 150$ K.

The low values of the order/disorder transition temperature $T_c$ in surface alloys compared to their bulk analogs can be rationalized by the lower coordination of the atoms in an ordered 2D alloy compared to a bulk alloy. This lower coordination reduces the energy loss associated with a defect in the ordered ground state structure, while for a comparable number of atoms the gain in configurational entropy is similar in 2D and in 3D phases. The small driving forces for ordering in the Cu$_x$Pd$_{1-x}$/Ru(0001) monolayer surface alloys and the resulting low order–disorder transition temperature provide a simple explanation for the absence of long-range ordered structures under experimentally accessible conditions, i.e., at temperatures, where adlayer equilibration is kinetically possible.
Figure 1.3.6 Simulated annealing of a monolayer CuPd/Ru(0001) surface alloy. (a) Distribution at 600 K; (b) mixing energy as function of temperature (decreasing from 600 K to 1K); (c) distribution at 1 K. From Ref. [62].
The tendency towards ordering is particularly low on hexagonally packed surface alloys with dominant nearest-neighbour interactions because of the relatively high degeneracy of different structures with similar compositions [5, 89]. The difference between a quadratic vs. a hexagonal packing is evident for Pb/Cu(100) vs. Pb/Cu(111): only the former tends to form long-range ordered Type I alloys [23]. A more pronounced stabilization of ordered bimetallic surfaces with hexagonal packing can be attained on ordered bulk alloys as Pt$_x$Sn$_{1-x}$ [90], where the surface ordering is supported by the long-range order in deeper layers. In Sn containing systems, also surface alloys with long-range order were described [91–94]. Likewise, Type III surface alloys with a large size mismatch of the two guest species have a higher tendency towards periodic 2D ordering [95]. For 2D alloys fabricated by thermally activated intermixing one will generally have to expect a lower degree of lateral order due to thermal excitation.

1.3.6 Reality Check: Predict and Verify Lateral Atom Distributions

As mentioned, the EPI parameters needed for MC simulation of the atom distribution in 2D alloys can also be determined by fitting to the results of DFT calculations. Those results are the energies of a number of periodically ordered surface alloys. The basic idea is that the energy trends observed for such ordered alloys also contain information about the behaviour of disordered alloys (see Chapter ... in Volume 3). The higher the variety of compositions and atom arrangements of/in the unit cells, the more information is contained in those data. Obviously, the number of calculated structures must exceed the number of required EPI parameters. Using Au$_x$Pt$_{1-x}$/Pt(111) as an example, a simplified procedure to determine EPI parameters based on a set of DFT based energies will be explained and demonstrated in the following.

Using the Vienna ab initio simulation package (VASP) [96] one can calculate the total energies of ordered Au$_x$Pt$_{1-x}$/Pt(111) slabs. In the case shown here, 41 ordered Au$_x$Pt$_{1-x}$/Pt(111) structures were used.
as input [52]. The surface alloys are represented by Au, Pt, or Au$_x$Pt$_{1-x}$ monolayers on top of five-layer Pt(111) slabs. The overlayers as well as the two underlying Pt layers are allowed to relax vertically and laterally. Depending on the Au : Pt ratio, the unit cells of the periodically repeated slabs had the lateral dimensions (4 × 4), (√7 × √7), (3 × 3), (2 × 2), (√3 × √3), or (2 × 1). A few selected examples are depicted in Figure 1.3.7, along with the calculated energies. The precision of DFT based energies obtained this way can be estimated to be ~ ±10 meV.

![Figure 1.3.7](image)

**Figure 1.3.7** Left: ordered Au$_x$Pt$_{1-x}$/Pt(111) surface alloys, together with the mixing energies as derived from DFT results. Right: Pure metals.

Starting from the total energies of the different slabs, which include pure Pt slabs and complete Au monolayers, one can calculate the mixing energies of a structure $\alpha$ via
\[ \Delta H_{\text{mix}}(\alpha, \text{DFT}) = E(A_xB_{1-x} / C) - (x_A \cdot E(A_{\text{ML}} / C) + x_B \cdot E(B_{\text{ML}} / C)) \]
\[ = E(A_xB_{1-x} / C) - (x_A \cdot E(A_{\text{ML}} / C) + (1 - x_A) \cdot E(B_{\text{ML}} / C)) \]

or, specifically for Au$_x$Pt$_{1-x}$/Pt(111)

\[ \Delta H_{\text{mix}}(\alpha, \text{DFT}) = E(Au_xPt_{1-x} / Pt(111)) - (x_{Au} \cdot E(Au_{\text{ML}} / Pt(111)) + (1 - x_{Au}) \cdot E(Pt(111))) \]

For a given ordered Au$_x$Pt$_{1-x}$/Pt(111) surface alloy, this expresses the difference in potential energy with respect to two separate phases consisting of only Au or Pt in the outermost layer, without any boundaries. Calculation of the EPI parameters requires an expression for this mixing energy which is based on these EPI parameters, i.e., the 2D lattice-gas Hamiltonian

\[ H\left(\{R_i\},\{s_i\}\right) = \frac{1}{2} \sum_{R_i} \sum_{R_j} V_{\text{EPI}}(r_{ij}) s_i s_j , \quad (5) \]

which then yields

\[ \Delta H_{\text{mix}}(\alpha, \text{EPI}) = H(\alpha, \text{EPI}) - H(\text{phase separated}, \text{EPI}) \]
\[ = \frac{1}{2} \sum_{R_i} \sum_{R_j} V_{\text{EPI}}(r_{ij}) s_i s_j - \left( x_A \cdot \frac{1}{2} \sum_{R_i} \sum_{R_j} V_{\text{EPI}}(r_{ij}) \cdot 1 + (1 - x_A) \cdot \frac{1}{2} \sum_{R_i} \sum_{R_j} V_{\text{EPI}}(r_{ij}) \cdot 1 \right) \]
\[ = \frac{1}{2} \sum_{R_i} \sum_{R_j} V_{\text{EPI}}(r_{ij}) s_i s_j - \frac{1}{2} \sum_{R_i} \sum_{R_j} V_{\text{EPI}}(r_{ij}) \]

where \( i \) and \( j \) run over all sites in the unit cell, and \( r_{ij} \) denotes the distance between those sites, which in turn determines \( V_{\text{EPI}}(r_{ij}) \) (see above). The first double-sum \( H(\alpha, \text{EPI}) \) in this expression contains the information about the atom distribution within the unit cell of structure \( \alpha \), which determines for how many couples of sites \( i \) and \( j \) within the unit cell the product \( s_i s_j \) is +1 and -1, respectively. Since the reference structures with only A or B in the outermost layer do not have unlike neighbours, the product
s_{i,j} is always +1 in that sum, which simplifies the second double-sum H(phase separated,EPI). For example, if only on a hexagonal lattice EPIs up to the 5th neighbour are considered, we get

$$H(\text{phase separated,EPI}) = 3 \cdot V_{\text{EPI}(1)} + 3 \cdot V_{\text{EPI}(\sqrt{3})} + 3 \cdot V_{\text{EPI}(2)} + 6 \cdot V_{\text{EPI}(\sqrt{7})} + 3 \cdot V_{\text{EPI}(3)} \quad (8a)$$

for a pairwise interaction model that only includes neighbours in a distance of 1, $\sqrt{3}$, 2, $\sqrt{7}$, and 3 (see Figure 1.3.2). In total, we can write the mixing energy $\Delta H_{\text{mix}}(\alpha,\text{EPI})$ of any structure $\alpha$ as weighted sum of the $V_{\text{EPI}}$ according to

$$\Delta H_{\text{mix}}(\alpha,\text{EPI}) = \sum_{r} k_{r}^{\alpha} \cdot V_{\text{EPI}(r)}, \quad (9)$$

where $r$ runs over all "shells" that are included in the respective EPI models and $k_{r}^{\alpha}$ is the weighting factor for the energy contribution $V_{\text{EPI}(r)}$.

Some typical structures ($\alpha$, $\beta$, $\gamma$, ...) and the corresponding mixing energies as determined by DFT are shown in Figure 1.3.7. The two homogeneous surfaces on the right-hand side represent the pure phases that are needed as reference points to calculate the mixing energies. In the best case, the fitted set of EPIs yields the same mixing energies as the DFT calculations themselves, which would mean that the following equation is fulfilled:

$$K \cdot \vec{V} = \vec{H} \quad (10a)$$
Since the matrix $K$ will generally not be a quadratic one, and since the EPI model will surely not be able to reproduce the DFT based mixing energies, however, the EPI parameters contained in vector $\tilde{V}$ have to be calculated via the pseudo inverse matrix, i.e., a least-squares fit according to

$$\tilde{V} = (K^TK)^{-1} \cdot K^T \cdot \tilde{H}$$

(11).

Based on the DFT results for the 41 different structures mentioned above, this yielded $V^{EPI}(1) = -11.5$ meV, $V^{EPI}(\sqrt{3}) = 1.3$ meV, $V^{EPI}(2) = 3$ meV, $V^{EPI}(\sqrt{7}) = 0$ meV, and $V^{EPI}(3) = 1.8$ meV. The results are plotted in Figure 1.3.8, together with the EPI values determined by fitting to the STM data to which they obviously agree quite well.

![Figure 1.3.8 Comparison of EPI parameters determined by fitting to DFT calculations and statistical STM evaluation. From Ref. [97].](image-url)
Figure 1.3.9 Direct comparison of measured (a-c) and MC simulated (d-f) Au\textsubscript{x}Pt\textsubscript{1-x}/Pt(111) surface alloys with three Au contents (as indicated). The MC simulation made use of the DFT-based EPI parameters.

The simulation not only correctly predicts the tendency towards 2D clustering, but also seems to yield a similar amount of Pt or Au monomers diluted in the respective other metal according to visual inspection. For a quantitative visualization of the agreement between simulation and experiment, Figure 1.3.10 and Figure 1.3.11 show some statistic evaluations of both data sets. The thick grey lines reflect ensemble averages obtained by MC simulation of 100 different Au\textsubscript{x}Pt\textsubscript{1-x}/Pt(111) surface alloys with 0<x\textsubscript{Au}<1. Figure 1.3.10 considers compact ensembles of 2…5 atoms including different numbers of Pt and Au atoms. The experimentally determined data points are in very good agreement with the MC based numbers. The right column of this graph highlights how much those simulated probabilities are different from those one would expect for random distributions. Figure 1.3.11 shows the average number of Au atoms around a given Au (a) or Pt (b) atom. Again, simulated and experimental values clearly differ from random distributions (dashed lines). The pairwise interaction model and the
determination of the EPIs from a small set of DFT calculated structure patterns is a gross simplification of what is state-of-the-art in theoretical surface science (Chapter Kerscher Müller, this Volume).

Nevertheless, the attainable degree of accuracy is sufficient to predict the most important features of this surface alloy as far as its adsorption and chemical properties are concerned.

Figure 1.3.10 Probabilities of compact (a) 2-, (b) 3-, (c) 4-, and (d) 5-fold ensembles (as displayed in the figure) to contain certain numbers of Pt and Au atoms (see legend), plotted as a function of Au content $x_{\text{Au}}$. Left column: experimentally counted (symbols) and simulated (thick lines) probabilities; right hand side: probabilities simulated for $\text{Au}_{x_{\text{Au}}-y_{\text{Au}}}/\text{Pt}(111)$ (thick lines) and curves for a random distribution (thin lines). From Ref. [52].

Figure 1.3.11 Counted average numbers of Au neighbors around a given Au or Pt atom (symbols: experiment; thick lines: MC simulation; thin dotted lines: random distribution). From Ref. [52].
1.4 Further Reading

Deeper insights about the thermodynamic properties of surface alloys, together with many examples from experimental and theoretical studies, can be found in ref. [1] and in the various chapters in ref. [98]. A comprehensive overview of surface segregation energies for many host/guest combinations can be found in refs. [4] and [6]. These tabulated values allow good predictions as to whether or not a given host/guest metal combination will form surface alloys that are metastable against bulk dissolution. Ref. [4] also provides a first idea about the lateral atom distribution one would have to expect for a given combination. For a comprehensive overview of sub-surface alloys and their properties, the reader is referred to Refs. [24], [44], and [99]. Chapter 8 of Volume 2 of this book describes many atomic scale processes that are not only important for chemically pure surfaces but also for the formation of surface alloys. Excellent descriptions of theoretical and computational concepts related to bimetallic systems can be found in Chapter XXX (Müller) of this Volume and in refs. [1], [4], [6], [80], [89], [98], and [100].

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1.6 References


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