The interplay of surface segregation and atomic order in alloys

Micha Polak, Leonid Rubinovich

Department of Materials Engineering, Ben-Gurion University of the Negev,
Beer-Sheva 84105, Israel
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Micha Polak*, Leonid Rubinovich

Department of Materials Engineering, Ben-Gurion University of the Negev, Beer-Sheva 84105, Israel

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Abstract

Surface segregation and related phenomena in alloys with long-range order (LRO) or short-range order (SRO) are reviewed with emphasis on prominent deviations from the well-known behavior of random solid-solutions. Issues concerning the competition between segregation and ordering tendencies, such as segregation suppression manifested in peaked equilibrium–segregation vs. temperature curves, on the one hand, and the disruption of near-surface LRO, on the other hand, are addressed in some detail. The pertinent roles of segregation entropy and segregation energy are considered for the cases of endothermic and exothermic processes. Besides surface-induced disorder (SID), effects of segregation on surface order–disorder transitions that can promote surface-induced order (SIO) are discussed. Several theoretical treatments based on the Ising model Hamiltonian energetics and on a number of statistical-mechanical approximations, including the Bragg–Williams, the cluster variation and the free-energy expansion methods, as well as Monte-Carlo simulations, are introduced and compared to experimental results reported mainly during the last decade. Segregation/ordering phenomena in thin films and nano-particles are addressed as well. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Surface segregation, manifested as intrinsic deviations of the solid–vacuum interfacial composition from the bulk value, is very common in metallic alloys (and in other multi-component materials). The subject has drawn much scientific attention mainly because of direct relevance to technology-related physical and chemical properties of surfaces. This includes oxidation/corrosion resistance, catalysis, electronic, magnetic, and adhesion properties, etc. [1,2]. All these practical implications are beyond the scope of this review, which focuses mainly on theoretical physical aspects of segregation in alloys exhibiting also ordering tendencies, and on some relatively recent experimental results.

Surface segregation in solid-solutions has been studied extensively since the late sixties. Much less attention has been paid to possible effects of short-range order (SRO) and to surface segregation in
alloys with long-range order (LRO). Several factors, such as geometrical parameters, chemical bond strength or the energy band structure, determine the atomic arrangement in the latter class of materials [3,4]. Although the report focuses mainly on surfaces of macroscopic single-crystal b.c.c. and f.c.c. solid-solutions and ordered alloys, the general theoretical approaches reviewed here allow predicting segregation/ordering characteristics in other systems, such as Laves phases as well as thin films and nano-particles, that usually exhibit distinct (sample) size effects.

The interdependence of surface segregation and LRO, or SRO, can manifest itself in a diversity of phenomena, such as segregation suppression and increase of the segregation levels with temperature, oscillatory segregation profiles, surface-induced order (SIO) and surface-induced disorder (SID). Since the interplay of segregation and ordering phenomena (LRO, in particular), is quite common in metallic systems, and in view of significant developments during the past decade, there appears now a genuine need for a comprehensive review of this issue. Equilibrium segregation phenomena of metallic constituents, including the role of thermal disordering, are accentuated here without relating in any detail to non-metal impurity segregation, or to aspects of segregation kinetics.

It should be noted that “surface” segregation extends beyond the outermost atomic layer, especially in solid-solutions, so that compositional variations include several layers underneath. Detailed experimental determination of the segregated multilayer is not an easy task. Conventional surface analysis techniques, such as Auger electron spectroscopy (AES) or X-ray photoelectron spectroscopy (XPS), often used in segregation studies, are not strictly surface specific, and the detected signal intensity is a superposition originating from a number of atomic layers, yielding some average composition throughout the characteristic probing depth. Hence, determination of the actual composition gradient by means of XPS or AES requires quite elaborate procedures, and even then the limited depth resolution cannot yield the desirable atomic layer-by-layer information from the shallow surface region. Several less common techniques, like ion scattering spectroscopy (ISS) or atom-probe field-ion microscopy (APFIM) are more surface specific and suitable to segregation studies, as will be demonstrated for ordered alloys in Section 4. In addition to quantitative compositional information they can furnish surface plane structural information, accessible also by low-energy electron diffraction (LEED). The principles and capabilities of these techniques can be found in numerous reviews and textbooks [5,92].

The theoretical descriptions of surface segregation in metallic alloys has two main aspects: (i) the microscopic or atomistic segregation energetics based on some interaction model or electronic-structure first-principles, and (ii) the segregation equilibrium state of the macroscopic system described by means of a statistical-mechanical approximation or Monte-Carlo simulations. The analogy between segregation profiles and LRO is helpful in adaptation of statistical-mechanical methods for characterization of bulk order to surface segregation theory that includes their interdependence. Both phenomena originate from interatomic interactions and manifest themselves as deviations from the average concentration of the solid. Similarly to LRO, the profiles include entire lattice layers parallel to the surface, creating in this manner a sort of near-surface “superstructure”.

Early experimental data on surface segregation phenomena in solid-solutions were analyzed by means of the Langmuir–McLean theory [6]. This simplistic approach predicts monolayer segregation that decreases monotonously with temperature, and enabled to derive “segregation enthalpy” from experimental surface compositions. However, this theory cannot account for the more diverse and complex multilayer segregation in real alloys with interaction-induced ordering tendencies. Thus, together with the development of experimental techniques and the fast increase of relevant data
(as reviewed recently by Bardi [7]), more elaborate theoretical approaches to surface segregation phenomena became necessary. Ising model type of descriptions allowed considering effects of interatomic interactions in terms of nearest neighbor pair-bonding. Such an approach became common when the Bragg–Williams (BW) theory, assuming random distribution of atoms at identical lattice sites, was adapted to describe multilayer surface segregation. It allowed calculating oscillatory segregation profiles in alloys with ordering tendency [8,9], and served as a starting point for theoretical studies of LRO/segregation interrelations [10,11]. This issue was considered also in studies that went beyond the BW approximation [12,13]. Likewise, basic SRO effects were accounted for by means of the cluster variation method (CVM) [13–18], the free-energy expansion method [19,20] or Monte-Carlo simulations [21–33], that can consider also possible contributions of atomic vibrations and surface relaxation [29]. Recent theories of surface segregation involve electronic structure calculations [34,35]. In his review Modrak [36] focused on the dependence of surface segregation on the microscopic electronic structure of alloys and discussed the coupling between segregation and ordering effects. A comprehensive account of different first principle approaches to the relationship between the electronic structure of a random binary alloy and its thermal equilibrium surface segregation has been given by Monnier [37]. Yet, basic effects of atomic long-range or short-range order on surface segregation in binary metallic alloys can be accounted for in terms of the pair-bond approach. Therefore, we have chosen to focus mainly on the corresponding thermodynamical and statistical-mechanical concepts and approximations based on the Ising model energetics. The report is organized as follows: following this introduction, occupation probabilities and correlation parameters are defined, as well as basic parameters characterizing surface segregation and the state of order (SRO and LRO) in a binary alloy. Section 3 deals mainly with theories of equilibrium surface segregation based on statistical-mechanical approximations (BW and beyond) for the alloy free-energy. Changes of equilibrium surface composition with temperature are discussed in relation to exothermic and endothermic segregation processes. Section 4 reviews the characteristics of surface segregation in ordered alloys, including recent experimental results. It deals with the basic surface equilibrium termination and its evolution with temperature in various types of ordered alloys. In Section 5 short-range order effects on surface segregation in solid-solutions are considered on the basis of a qualitative assessment of surface and bulk related perturbations in the total free-energy. In addition, theoretical predictions based on the free-energy expansion approach are compared quantitatively with experimental data and verified by recent results of Monte-Carlo simulations. Finally, a separate Section 6 is devoted to the issue of order–disorder phase transitions that are characteristic to surfaces and affected by segregation. The phenomena of surface induced disorder (SID) and surface induced order (SIO), including their occurrence in alloy thin films and nano-particles, are discussed. A detailed summary concludes the report.

2. Parameters pertinent to surface segregation and the state of order in a binary alloy

In ideally random A–B alloy, the probability of finding atom A does not depend on a particular lattice site or its surroundings, and is equal to the average concentration. Such completely disordered state can exist only when the segregation driving force and ordering driving forces due to interatomic interactions are very weak compared to the thermal energy. At lower temperatures (or for larger values of the energetic parameters) the surface composition can deviate from the bulk value, namely, segregation occurs. Moreover, usually A atoms tend to be preferentially surrounded by B atoms
2.1. Occupation probabilities and correlation parameters

A configuration $K$ of a binary alloy $A_iB_{1-c}$ can be characterized in the Ising model approach (Section 3.2) by set of spin-like variables $\{\sigma_i\}$, where $\sigma_i$ is equal to 1(−1) if the site $i$ is occupied by an atom of type $I=A(B)$. The occupation numbers, $\delta^I_i$, equal to 1(0) if an atom of the type $I$ does (not) occupy the lattice site $i$, are defined as

$$\delta^A_i = \frac{1 + \sigma_i}{2} \quad \text{and} \quad \delta^B_i = \frac{1 - \sigma_i}{2}. \quad (2.1)$$

The occupation probabilities of lattice sites $i_1,i_2,\ldots,i_n$ by atoms of types $I_1,I_2,\ldots,I_n$ are the statistical averages

$$p_{i_1i_2\ldots i_n}^{I_1I_2\ldots I_n} = \langle \delta^I_{i_1} \delta^I_{i_2} \ldots \delta^I_{i_n} \rangle. \quad (2.2)$$

Due to interatomic interactions, occupations of different lattice sites are not statistically independent, and Eq. (2.2) cannot be factorized, namely,

$$p_{i_1i_2}^{I_1I_2} = p_{i_1}^{I_1}p_{i_2}^{I_2} + \varepsilon_{i_1i_2}^{I_1I_2}, \quad p_{i_1i_2i_3}^{I_1I_2I_3} = p_{i_1}^{I_1}p_{i_2}^{I_2}p_{i_3}^{I_3} + p_{i_1}^{I_1}p_{i_2}^{I_2}e_{i_1i_2i_3}^{I_1I_2I_3} + p_{i_1}^{I_1}e_{i_2i_3}^{I_2I_3} + e_{i_1i_2i_3}^{I_1I_2I_3}, \ldots, \quad (2.3)$$

where interatomic correlation parameters, $\varepsilon_{i_1i_2\ldots i_n}^{I_1I_2\ldots I_n}$, are introduced as

$$\varepsilon_{i_1i_2\ldots i_n}^{I_1I_2\ldots I_n} = \langle \langle \delta^I_{i_1} - \langle \delta^I_{i_1} \rangle \rangle \langle \delta^I_{i_2} - \langle \delta^I_{i_2} \rangle \rangle \ldots \langle \delta^I_{i_n} - \langle \delta^I_{i_n} \rangle \rangle \rangle. \quad (2.4)$$

Since in a binary alloy $\delta^B_i = 1 - \delta^A_i$ and $\delta^B_i - \langle \delta^B_i \rangle = -(\delta^A_i - \langle \delta^A_i \rangle)$, all $p_{i_1i_2\ldots i_n}^{I_1I_2\ldots I_n}$ and $\varepsilon_{i_1i_2\ldots i_n}^{I_1I_2\ldots I_n}$ can be expressed via the occupation probabilities $p_{i_1i_2\ldots i_n}^{AA\ldots A}$ and the correlation parameters $\varepsilon_{i_1i_2\ldots i_n}^{AA\ldots A}$ of the $A$ atoms,

$$p_{i_1i_2\ldots i_n} = \frac{1}{2^n} \langle (1 + \sigma_{i_1})(1 + \sigma_{i_2})\ldots(1 + \sigma_{i_n}) \rangle, \quad (2.5)$$

$$\varepsilon_{i_1i_2\ldots i_n} = \frac{1}{2^n} \langle (\sigma_{i_1} - \langle \sigma_{i_1} \rangle)(\sigma_{i_2} - \langle \sigma_{i_2} \rangle)\ldots(\sigma_{i_n} - \langle \sigma_{i_n} \rangle) \rangle. \quad (2.6)$$

For example,

$$p_i^B = \langle 1 - \delta^A_i \rangle = 1 - p_i, \quad (2.7)$$

$$p_{ij}^{AB} = \langle \delta^A_i (1 - \delta^A_j) \rangle = p_i - p_{ij}, \quad (2.8)$$

$$p_{ij}^{BB} = \langle (1 - \delta^A_i)(1 - \delta^A_j) \rangle = 1 - p_i - p_j + p_{ij}, \quad (2.9)$$

$$\varepsilon_{ij} = \varepsilon_{ij}^{BB} = -\varepsilon_{ij}^{AB}. \quad (2.10)$$

As can be seen from Eq. (2.4), the parameters $\varepsilon_{i_1i_2\ldots i_n}^{I_1I_2\ldots I_n}$ characterizing interatomic correlations at short distances (SRO), are related to deviations of occupation numbers from their statistical averages, namely, to local compositional fluctuations. They are zero in case of perfect order (very low
temperatures) or complete disorder (very high temperatures), while the maximal absolute values are achieved in the order–disorder phase transition region (Fig. 1). An example for calculated and observed SRO at the Ni$_3$Pt (111) surface is shown in Fig. 2.

2.2. Order parameters

The sublattice and depth of a layer determine, in ordered alloys, the probability of finding atomic species at some lattice site. A set of layer and sublattice concentrations (probabilities) completely characterizes the segregation depth profile and LRO. Yet, the state of atomic order is conveniently described by layer-dependent LRO parameters defined below. Similarly, SRO parameters are used along with multi-site correlations (defined by Eq. (2.4)), that provide comprehensive description of compositional fluctuations.

In spite of their common origin, related to interatomic interactions, a segregation profile differs from bulk superstructure (LRO) since the surface breaks the crystal symmetry at any temperature (the symmetry of the alloy bulk can decrease by a transition from a high- to a low-temperature phase). In this sense surface segregation profiles resemble SRO, including the short-range depth.

In an ordered alloy with average concentration $c$, there are $m–1$ independent bulk LRO parameters, related to the concentrations $p^\lambda$ on $m$ bulk sublattices ($\lambda$ denotes the sublattice number). In a superstructure with two sublattices $\alpha$ (A atoms) and $\beta$ (B atoms), one bulk LRO parameter ($\eta$) is...
sufficient, and defined according to

\[ P^\alpha = c + \psi^\beta \eta \quad \text{and} \quad P^\beta = c - \psi^\alpha \eta, \tag{2.11} \]

where \( \psi^\alpha \) and \( \psi^\beta \) are the concentrations of lattice sites of the corresponding sublattices. For example, \( P^\alpha = c + \frac{3}{4} \eta \) and \( P^\beta = c - \frac{1}{4} \eta \) for the superstructure \( L1_2 \) (Fig. 3). In the disordered phase \( \eta \) vanishes (and \( P^\alpha = P^\beta = c \)). \( \eta = 1 \) corresponds to perfect long-range order (\( T = 0 \)). The superstructure DO\(_3\) (see Fig. 3) represents a case of ordered phase with three sublattices, characterized by two bulk LRO parameters, 

\[ \begin{align*}
  &P^\alpha = c + \frac{1}{4} \eta_1 + \frac{1}{2} \eta_2, \\
  &P^\beta = c + \frac{1}{3} \eta_1 - \frac{1}{2} \eta_2 \quad \text{and} \quad P^{\gamma} = c - \frac{1}{4} \eta_1.
\end{align*} \]
Turning to ordered alloy surfaces, depending on the orientation, one or more bulk-truncated terminations can occur at equilibrium (Section 4.1). For example, there is a single surface termination in $L_1(111)$ (Fig. 3c) and $B_2(110)$, whereas for the orientations $L_1(100)$, $L_1(110)$ (Fig. 3a,b) and $B_2(100)$ two terminations are possible. Since due to surface segregation the concentration depends on the depth of the layer, plane-related LRO parameters (for layers containing sublattices) can be introduced. For example, in-plane LRO parameter, $\eta_q$, for mixed $q$-layer (100) in $L_1$ or (110) in $B_2$ is given by $P^a_q = c_q + \frac{1}{2} \eta_q$. Moreover, depending on the surface orientation, near-surface concentrations in ordering alloy oscillate in depth, as will be discussed in Section 6.2. These oscillations should decay in the case of single surface termination (Fig. 3c), since layer concentrations in the bulk are equal. For surface orientations allowing more terminations (Fig. 3a,b), LRO-related oscillations in the bulk prevail.

Since the f.c.c. lattice is composed out of four interpenetrating simple cubic sublattices, the corresponding fractional occupation numbers $x_1, x_2, x_3, x_4$ can be considered, as well as the Landau–
The order parameter field 
\[ \psi_1 = x_1 - x_2 - x_3 + x_4, \quad \psi_2 = x_1 - x_2 + x_3 - x_4, \]
\[ \psi_3 = x_1 + x_2 - x_3 - x_4, \quad \psi_4 = x_1 + x_2 + x_3 + x_4. \]

The order parameter \( \psi = (\psi_1 \psi_2 \psi_3) = (111), (\bar{1}11), (\bar{1}1\bar{1}) \) and \( (1\bar{1}\bar{1}) \) (Fig. 4) describes four ordered states of the structure \( L1_2 \), which occur with equal probability in the bulk (separated by antiphase boundaries). Since the symmetry between these states is broken at the surface, the multi-component order parameter field is useful for segregation/ordering description in alloys (Section 6.2, [42]).

Definition of the SRO parameters, such as done by Bethe or Cowley, is mainly a matter of convention [43,44]. Specifically, in the case of surface segregation layer-dependent SRO parameters were defined in [12,13]. For example, for \( B2(110) \) the intralayer and interlayer SRO parameters are, respectively, [12]:

\[ \sigma_{qq} = \frac{P_{qq}^x - c_q^2}{c_q(1 - c_q)} \quad \text{and} \quad \sigma_{pq}^x = \frac{P_{pq}^x - c_p c_q - \frac{1}{2} \eta_p}{c_p(1 - c_q)}, \quad \sigma_{pq}^\beta = \frac{P_{pq}^{\beta x} - c_p c_q + \frac{1}{2} \eta_p}{c_p(1 - c_q)}. \]

An average SRO parameter between the \( p \)th and \( q \)th layer can be defined by \( \sigma_{pq} = \frac{1}{2} (\sigma_{pq}^x + \sigma_{pq}^\beta) \).

Usually, SRO parameters are introduced in such a way that, unlike the correlation parameters (Section 2.1), they do not necessarily decrease at low temperatures. On the other hand, unlike LRO parameters,
they do not vanish at the order–disorder transition temperature. Examples for the dependence of LRO, SRO and surface concentration on temperature will be given in Section 4.

3. Theories of equilibrium surface segregation in alloys

Diverse theoretical approaches to equilibrium segregation of alloy clean surfaces are reviewed here, without relating to external factors such as selective chemisorption, ion bombardment, etc. The first theoretical description of surface segregation phenomena was given by Gibbs, who introduced the adsorption isotherm [45]

\[ \Gamma_A = -\left( \frac{\partial \gamma}{\partial \mu_A} \right)_{T,p}, \]

which links the surface excess of constituent \( A (\Gamma_A) \) in an \( A-B \) binary system with the surface energy (\( \gamma \)) and the chemical potential of \( A (\mu_A) \). The sign minus in Eq. (3.1) shows that surface enrichment of a constituent is associated with a decrease of the surface energy. Alternative, more useful descriptions of surface segregation are based on specific models for the alloy energetics and application of statistical-mechanical approximate methods.

3.1. Surface segregation driving forces

In an early approach to the interface–bulk equilibrium in a binary solid-solution \( A_cB_{1-c} \), the Langmuir model for adsorption [46] was extended by McLean to segregation at grain-boundaries [6]. In this simplistic approach the surface was modeled as a set of equivalent atomic sites with a binding energy that is different from that of the bulk. Moreover, effective interatomic interactions and multilayer segregation were ignored. The classical form of the so-called Langmuir–McLean equation often described quite successfully the temperature dependence of segregation,

\[ \frac{c_0}{1-c_0} = \frac{c}{1-c} \exp \left( -\frac{\Delta F_{ex}^0}{RT} \right), \]

where \( c_0 \) and \( c \) are, respectively, the surface and bulk concentrations of element \( A \), and \( \Delta F_{ex}^0 \) is the excess free energy of segregation (discussed in some detail in Section 3.6).

Later, nearest neighbor interactions were taken into account, while retaining the equivalent site assumption, as in the approach of Fowler and Guggenheim [47]. The excess entropy of segregation, \( \Delta S_{ex}^0 \), as part of the excess free energy, \( \Delta F_{ex}^0 = \Delta U_0 - T\Delta S_{ex}^0 \) (see Section 3.6), was often ignored, while three contributions to the segregation energy, \( \Delta U_0 \), were commonly considered in the prediction of monolayer segregation driving forces [48] in a substitutional solid-solution,

\[ \Delta U_0 = (\gamma_A - \gamma_B)\omega + \frac{2\Delta E_m}{zc(1-c)} \left[ z_l(c-c_0) + z_v \left( c - \frac{1}{2} \right) \right] + \Delta H_{sm}^0. \]

- The first term involves the difference of surface tensions of the pure elemental components, multiplied by the surface area per atom.
The second term represents effects due to interactions between the two components; $\Delta E_m$ is the energy of mixing, and $z$, $z_1$ and $z_v$ are, respectively, the coordination number in the bulk, the number within the first layer and with respect to the second layer. These two term contributions constitute what is usually referred to as the “bond-breaking” model.

The third term represents contribution arising from the complete release upon segregation of bulk elastic strain energy due to solute–solvent atomic size mismatch effects.

The three-contribution approach was generalized to a more realistic multilayer treatment of interaction-induced in-depth segregation profiles, by means of the regular solution model corresponding to the Bragg–Williams approximation (see Section 3.3). These approaches suppose fixed positions of interacting atoms in sites of a rigid lattice, like in the Ising model (Section 3.2). In many early works, the release of strain energy due to segregation of a solute atom at the surface of (dilute) solid-solution was roughly approximated from linear elastic continuum theory [48,49]. However, the validity of the continuum theory for atomic-scale related estimations is quite questionable. Moreover, since the size mismatch energy can be part of the experimentally measured heat of mixing, a suitable correction [50] should be taken into account in case the pair-wise interactions are obtained from bulk thermodynamic data [12,51]. There were also attempts to estimate relaxation of the strain energy upon segregation, namely, its residual (non-zero) surface value [52], or to derive a more reasonable value from a fit to experimental data [53,19]. Furthermore, elastic energy release can occur also for deeper layers ($\Delta H_{s_{m}}^{s_{m}} > 0$). The size effect can be more accurately described by using atomistic models with relaxation [21,54,55] to minimize the strain energy in the dilute limit, from which $\Delta H_{s_{m}}^{s_{m}}$ can be interpolated for intermediate concentrations. Problems in the “bond breaking” model, such as surrounding–independent pair bonding, or the inclusion of lattice strain energy and its possible relaxation upon segregation, have stimulated the application of the embedded atom method (EAM) [23,24] (Section 3.7) and its modified version (MEAM) [56,57].

The interdependence of electronic structure and surface segregation was reviewed recently by Modrak [36] and by Monnier [37]. Since a genuine first-principle calculation of the free-energy (and its consequent minimization) cannot be done, the Ising model is commonly used to reduce the large number of configurations in a real alloy, and electronic structure calculations determine energetic parameters of the Ising Hamiltonian. Two methods are used currently to generate the corresponding parameters: the generalized perturbation method (GPM), was first applied to the surface segregation problem [58], within a simplified tight-binding (TB) model of the electronic structure, and later, it was improved at the semi-empirical level [59]. Another method [60] used first-principles to calculate the ground-state energy of ordered compounds for which correlation functions are particularly simple to evaluate and to determine effective cluster interactions. Approaches to the determination of the interaction parameters in the cluster expansions were reviewed by de Fontaine [61] and Zunger [62]. When energetic parameters of the Ising Hamiltonian are defined, methods of classical statistical mechanics can be adapted and applied to find the equilibrium near surface compositions and possible atomic order.

### 3.2. The Ising model Hamiltonian of a binary alloy with a surface

The Ising model for a binary $A–B$ alloy with rigid lattice and constant pair-interactions is used commonly in free energy calculations. The alloy configurational energy reads:

$$E = \sum_{(m,n)} (V_{mn}^{AA} s_m^A s_n^A + V_{mn}^{AB} s_m^A s_n^B + V_{mn}^{BA} s_m^B s_n^A + V_{mn}^{BB} s_m^B s_n^B),$$

(3.4)
where \( V_{mn}^{AA} \), \( V_{mn}^{BB} \), and \( V_{mn}^{AB} = V_{mn}^{BA} \), are the interaction energies between the corresponding atoms at site \( m \) and at site \( n \), \( \{mn\} \) denotes a pair of lattice sites and \( \delta^I \) are occupation numbers (Eq. (2.1)). Although the nearest-neighbor pair-interaction approximation is often used, the following derivation is more general and the interactions included in Eq. (3.4) are not restricted by interatomic distances. Using spin-like variables as in Eq. (2.1), the energy can be rewritten as

\[
E = E_0 + \frac{1}{2} \sum_m \left( \sum_{n(n\neq m)} \tau_{mn} \sigma_m \right) + \frac{1}{2} \sum_{\{mn\}} V_{mn} \sigma_m \sigma_n,
\]

where \( E_0 = \frac{1}{4} \sum_{\{mn\}} \left( V_{mn}^{AA} + V_{mn}^{BB} + 2V_{mn}^{AB} \right) \), \( \tau_{mn} = \frac{1}{2} \left( V_{mn}^{AA} - V_{mn}^{BB} \right) \), and \( V_{mn} = \frac{1}{2} \left( V_{mn}^{AA} + V_{mn}^{BB} - 2V_{mn}^{AB} \right) \).

The sum \( h_m = \sum_{n(n\neq m)} \tau_{mn} \) is equal for all bulk sites in the alloy (\( \equiv h_b \)), but it depends on the plane number \( p \) near the surface, \( h_p = h_b + \Delta h_p \), where \( \Delta h_p \) accounts for the difference in \( p \)-layer tensions between pure constituents. Since the total numbers of \( A \) and \( B \) atoms are constant, the configuration independent contribution, \( E_0 + \frac{1}{2} h_b (N_A - N_B) \), can be omitted. Hence, the equivalent Hamiltonian reads

\[
H = \frac{1}{2} \sum_p \left( \sum_{m \in p \text{-layer}} \Delta h_p \sigma_m \right) + \frac{1}{2} \sum_{\{mn\}} V_{mn} \sigma_m \sigma_n.
\]

The assumption of rigid lattice with pair-interactions is inadequate in case of large differences in atomic sizes between the two alloy constituents, so a size mismatch energy, \( \Delta H_p^{sm} \) (introduced in the previous section), can be included in the “layer field”,

\[
H_p = \frac{1}{2} \left( \Delta h_p + \Delta H_p^{sm} \right),
\]

at and near the surface. Thus, the Ising model Hamiltonian of a binary alloy with a surface reads

\[
H = \sum_p \left( \sum_{m \in p \text{-layer}} H_p \sigma_m \right) + \frac{1}{2} \sum_{\{mn\}} V_{mn} \sigma_m \sigma_n.
\]

Usually \( H_p \) is expected to differ from zero only at the outmost layer and perhaps several layers underneath, but in “size-factor” intermetallics the contribution of \( \Delta H_p^{sm} \) can be considerable for the smaller atom sublattice even in the bulk (Section 4.2).

3.3. The adapted Bragg–Williams approximation

The most common statistical-mechanical approach to surface segregation is based on the classical mean-field theory [44], which is equivalent to the Bragg–Williams (BW) approximation, assuming random distribution of atoms at identical lattice sites. The BW method for the alloy bulk with nearest neighbor interactions was first proposed by Gorsky [64] and further developed by Bragg and Williams [65]. For the sake of simplicity of notation, equivalency of all sites in the layer is supposed, but all formulas derived below can be easily generalized by additional summation over sub-lattices.

The BW approximation ignores fluctuations and interatomic correlations in the alloy (i.e., \( \epsilon_{i_1 i_2 \ldots i_n} \equiv 0 \)). Neglecting energy fluctuations means that the exponent in the partition function,
where \( Z = \sum_k \exp \left( -\frac{H}{kT} \right) \), can be taken outside the summation:

\[
Z^{BW} = \exp \left( -\frac{U^{BW}}{kT} \right) \sum_k^{BW} \exp \left( -\frac{U^{BW}}{kT} \right),
\]

(3.7)

where \( U^{BW} \) is the alloy energy in the BW approximation, and \( g^{BW} \) is the number of all possible configurations of atoms consistent with the set of concentrations \( c_p \) \((p = 0, 1, 2, \ldots)\) of layers having \( N_p \) sites,

\[
g^{BW} = \frac{N_p!}{(N_p c_p)! [N_p (1 - c_p)]!}.
\]

The BW free energy is then given by

\[
F^{BW} = -kT \ln Z^{BW} = U^{BW} - kT \ln g^{BW} = U^{BW} - TS^{BW},
\]

where the BW configurational entropy can be obtained by means of the Stirling’s approximation for the factorials

\[
S^{BW} = k \ln g^{BW} = -k \sum_p N_p (c_p \ln c_p + (1 - c_p) \ln (1 - c_p)).
\]

(3.8)

Since in the BW approximation \( \epsilon_{i_1 i_2 \ldots i_n} \equiv 0 \), statistical averages in Eq. (2.3) can be factorized, namely, \( p_{i_1 i_2 \ldots i_n} = p_{i_1} p_{i_2} \ldots p_{i_n} \) and \( \langle \sigma_i \sigma_j \rangle = \langle \sigma_i \rangle \langle \sigma_j \rangle = (2c_i - 1)(2c_j - 1) \). Averaging of the Ising Hamiltonian (3.6) gives the alloy BW energy:

\[
U^{BW} = \sum_p N_p H_p (2c_p - 1) + \frac{1}{2} \sum_{\{mn\}} V_{mn} (2c_m - 1)(2c_n - 1).
\]

(3.9)

Hence, the free energy of a semi-infinite alloy is in the BW approximation,

\[
F^{BW} = \sum_p N_p H_p (2c_p - 1) + \frac{1}{2} \sum_{\{mn\}} V_{mn} (2c_m - 1)(2c_n - 1)
+ kT \sum_p N_p (c_p \ln c_p + (1 - c_p) \ln (1 - c_p)).
\]

(3.10)

Differentiation with respect to \( c_p \) leads to a set of coupled exponential segregation equations (Section 3.5).

The free energy can be represented as the sum of the free-energy of an “ideal” solution (without any energetic contributions), \( F^{id} = -TS^{BW} \), and the energetic non-correlational contribution, \( \delta F^{BW} = U^{BW} \), with the “surface field”-related term, \( \delta F^{BW}_H \), and interaction-related term, \( \delta F^{BW}_V \), given respectively, by the first and second terms in Eq. (3.9).

Adding the SRO-related perturbation discussed in the next section, the overall contribution of interatomic interactions to the free-energy can be considered as composed of two terms,

\[
\delta F_V = \delta F^{BW}_V + \delta F^{SRO}_V.
\]

(3.11)

\( \delta F^{SRO}_V \) considers the non-randomness of the actual distribution of solute–solvent atoms \( \epsilon_{i_1 i_2 \ldots i_n} \neq 0 \) in a solid-solution or in sublattices of alloys with LRO.
3.4. Statistical-mechanical approximations beyond the Bragg–Williams theory: incorporation of short-range order

More accurate estimation of the alloy free energy is based usually on improved partition functions. The equilibrium value of any parameter or set of parameters, \( \bar{z} \), that characterizes an alloy corresponds to a minimum of the free energy, \( F_\bar{z} \). Depending on the problem to be solved and the statistical-mechanical method \( \bar{z} \) can include plane or sublattice concentrations, long-range order and short-range order parameters, etc. The free energy

\[
F_\bar{z} = -kT \ln Z_\bar{z}
\]

is then related to a partition function of “restricted” statistical ensemble with a specified (fixed) value of \( \bar{z} \):

\[
Z_\bar{z} = \sum_K \sum_\bar{z} \exp\left(-\frac{H}{kT}\right).
\]

(3.12)

The total partition function is

\[
Z = \sum_K \exp\left(-\frac{H}{kT}\right) = \sum_\bar{z} Z_\bar{z},
\]

(3.13)

were the summation goes over all possible configurations \( K \) and values of \( \bar{z} \). The BW approximation and other statistical-mechanical approaches discussed below assume that \( Z \) can be replaced by its maximal component, \( Z_\bar{z} \). It means neglecting possible fluctuations in \( \bar{z} \) (that can still exist in subsystems) and imposing certain constraints on the correlation parameters. For any interatomic interactions or temperature the “fluctuational” constraints are valid for a chosen statistical ensemble, and should be taken into account in all relevant calculations. The simplest example of such constraints can be obtained in the canonical statistical ensemble, where the number of \( A \)-atoms is constant, so that \( \langle (N_A - \langle N^A \rangle)^2 \rangle = 0 \). When we take into account that \( N^A = \sum_i \delta^A_{ij} \) and the definitions (2.2 and 2.3) the constraint regarding site probability and pair correlations, \( \sum_i P_i (1 - P_i) + \sum_{i,j; i \neq j} \delta_{ij} = 0 \) is obtained.

It should be noted that application of the BW approximation means the neglect of fluctuations in energy in a statistical ensemble “wider” than the microcanonical, since in the calculated number of configurations \( g^{BW} \) (see Eq. (3.8)), different energies are actually included. Alternatively, the BW theory can be considered as using microcanonical ensemble (in which the energy is specified), but with erroneous overestimated entropy. Statistical-mechanical methods aimed to improve the BW approximation are based on approximate calculation of a restricted partition function and can be subdivided into two groups: methods applying microcanonical statistical ensemble (“entropy methods”), and those involving the Kirkwood expansion method and its improved modifications (“fluctuating-energy methods”).

3.4.1. Methods based on improved derivation of the alloy entropy

While methods of this group can be introduced in the framework of a generalized mean-field theory, a more consistent formulation is based on approximations for the alloy free-energy [44], which calculate more accurately entropy in the microcanonical or even more “restricted” statistical ensemble. Actually, in such approaches the exponent, which is equivalent for all configurations, can be factored
out in (3.13) giving the following expression for the free-energy (3.12):

$$F_x = -kT \ln \sum_k \exp \left(-\frac{H}{kT}\right) = H_x - kT \ln g_x.$$ 

From Eq. (3.6) for the Ising model Hamiltonian, the alloy internal energy can be expressed via one-particle and pair occupation probabilities. In a more general case, effective cluster interactions beyond the nearest-neighbor interactions are considered [44,61]. Nevertheless, depending on the model, the internal energy is a rather simple function of occupation probabilities and correlation parameters, and can be specified together with them. A much more difficult problem is the derivation of a formula for the number of configurations \(g_x = \sum_k 1\) and the entropy \(S_x = k \ln g_x\). Efforts to solve it included the Bethe method [66] or the equivalent quasi-chemical approximation [47,67], and eventually the cluster variation method (CVM) emerged [68–70]. Comprehensive review of the cluster approach to order–disorder transformations in alloys can be found in [44,61], and its application to alloys with a surface in [16]. In the CVM formalism the alloy entropy is expressed approximately via successive partial entropies for a single lattice point \((p)\), a pair \((p,q)\) etc.:

$$S_p = -k \sum_{\sigma_p} \rho_1(\sigma_p) \ln \rho_1(\sigma_p), \quad S_{p,q} = -k \sum_{\sigma_p,\sigma_q} \rho_2(\sigma_p,\sigma_q) \ln \rho_2(\sigma_p,\sigma_q), \ldots,$$

where \(\rho_1(\sigma_p), \rho_2(\sigma_p,\sigma_q), \ldots\) are partial density functions [61] related to occupation probabilities and multi-site correlation parameters. The basic CVM assumption is that for large enough maximal clusters the alloy entropy can be calculated quite accurately since correlations over distances spanned by this cluster become negligibly small. It should be noted that such arguments are not valid near second-order transition where correlations extend to infinity. Minimization of the free-energy with respect to independent cluster probabilities or correlations produces a set of non-linear algebraic equations that must be solved simultaneously. Their number, as well that of the “fluctuational” constraints, grows exponentially with the number of lattice points in the cluster, and for ten points it becomes exceedingly large. Increasing the size or the number of maximal clusters can lead to results worse than within a CVM of lower order [44]. The point approximation, which corresponds to a cluster consisting of a single lattice point, is equivalent to the BW approximation. In case of b.c.c. structure the pair approximation corresponds to the Bethe approximation and gives a fairly reasonable result. A more advanced approximation, at least the tetrahedron approximation, is required for f.c.c. lattices [71]. It was first applied to the problem of surface segregation and disordering at the surface of f.c.c. ordered alloys by Kumar and Bennemann [13], and later in [14–17]. It was used also in calculation of (100) surface segregation profiles in Cu–Ni solid-solution [18].

It should be noted, however, that these correlation theories based on improved derivations of the alloy entropy, use much more complicated formulae for the alloy free energy than the BW theory. Furthermore, for the case of surface segregation even the simplest pair approximation explicitly includes a large number of intra-layer and inter-layer probabilities or SRO parameters. Due to such computational complications associated with the presence of a surface, these correlation approximations have been less frequently used than the BW approach.

### 3.4.2. Free energy expansion methods

When fluctuations in energy are taken into account in the corresponding statistical-mechanical ensemble, \(H\) is not equivalent for all lattice configurations and \(\exp(-H/kT)\) cannot be factored out in the
partition function. Therefore, Kirkwood proposed the inverse temperature cumulant expansion method (Section 3.4.2.1) for calculation of the free energy. It was developed originally for the descriptions of atomic and magnetic ordering in the bulk [72–77]. Recently, it was applied to the problem of surface magnetic order [78,79], and adapted to unravel the general role of SRO in surface segregation [19]. Advantages of this consistent approach include its general applicability to Ising systems, the relative simplicity of the equilibrium equations, the convenient extension to non-nearest neighbor interactions and its compatibility with the method of “area-preserving map” for quantitative evaluation of in-depth concentration gradients [54] (Section 3.5). Furthermore, since the actual free energy of a system does not always correspond to a single phase, and a more accurate calculation should include configurations of different phases or intermediate states [80], the use of a less restricted statistical ensemble in the Kirkwood approach can be preferable to the cluster-variation method. Moreover, the smaller number of parameters in such ensemble makes the free energy minimization easier. The Kirkwood approach is consistent in taking into account higher-order correlations, while in entropy methods choosing the best cluster can be problematic. In case of weak interatomic correlations all methods give similar predictions with some improvement over the BW approximation, but divergence of results of different approximations increases with the correlation strength. Of course, a criterion for accuracy of any approximation is the agreement with experimental data, or with predictions of a more accurate approach, such as Monte-Carlo simulations (Sections 3.7 and 5.3).

3.4.2.1. The inverse-temperature (cumulant) expansion. Free-energy expansion methods are appropriate for elucidation of SRO effects on surface segregation both below and above order–disorder transition. For the sake of brevity we omit the index \( a \) denoting the fixed layer or sublattice concentration, as in the partition function \( Z_a \) of a “restricted” statistical ensemble (Eq. (3.13)). It can be presented in the following form:

\[
Z = \sum_k \exp \left( -\frac{H}{kT} \right) \exp \left( -\frac{U_{BW}}{kT} \right) \sum_k \exp \left[ -\frac{(H - U_{BW})}{kT} \right] = g \exp \left( -\frac{U_{BW}}{kT} \right) \exp \left[ -\frac{(H - U_{BW})}{kT} \right] = Z_{BW}^{BW} \exp \left[ -\frac{(H - U_{BW})}{kT} \right],
\]

where \( g \) is the number of configurations in the statistical ensemble, \( Z_{BW}^{BW} \) is the partition function in the BW approximation, and \( \langle \ldots \rangle_0 \) denotes arithmetical average over the configurations. Hence, the SRO correction to the free-energy (Section 3.3) is given by [74],

\[
\delta F_{SRO} = -kT \ln \left( \exp \left( -\frac{\Delta H}{kT} \right) \right)_0,
\]

(3.15)

where

\[
\Delta H = H - U_{BW} = \frac{1}{2} \sum_{mn} V_{mn} \Delta \sigma_m \Delta \sigma_n,
\]

(3.16)

and

\[
\Delta \sigma_m = \sigma_m - \langle \sigma_m \rangle = \sigma_m - (2c_m - 1).
\]
Since the layer concentrations are specified (fixed), \( H_p(\sum_{m \in p \text{- layer}} \Delta \sigma_m) = 0 \), and \( \Delta H \) does not contain any contribution related to the "layer field", \( H_p \). Eq. (3.15) can be then expanded in series:

\[
\delta F^{\text{SRO}} = -kT \ln \left[ 1 + \sum_{s=1}^{\infty} \frac{\langle \Delta H^s \rangle_0}{s!} \left( -\frac{1}{kT} \right)^s \right].
\] (3.17)

The SRO correction to the free energy expanded in inverse-temperature power series is given in the \( n \)th order correlation approximation by

\[
\delta F_n^{\text{SRO}} = -kT \sum_{s=1}^{n} \frac{C_s}{s!} \left( -\frac{V}{kT} \right)^s,
\] (3.18)

where \( C_s \) are \( s \)th order cumulants. Evaluation of the cumulants is a laborious task, greatly facilitated by a graphical notation [74]. There are contributions to \( C_s \) proportional to the number of lattice sites, \( N \), and, due to the “fluctuational” constraints, also to \( N^{-p}(p = 0, 1, 2, \ldots) \). The latter should be taken into account only for nanoparticles and can be neglected for large \( N \) values.

Since

\[
C_1(\Delta H) = \langle \Delta H \rangle_0 = \langle H \rangle_0 - U^{\text{BW}} = 0,
\]

the first SRO correction \( \delta F_1^{\text{SRO}} = 0 \). The lowest non-zero correction originates from the second cumulant [74]:

\[
C_2(\Delta H) = \frac{1}{4} \sum_{\{mn\}} V_{mn}^2 \langle \Delta \sigma_m^2 \rangle_0 \langle \Delta \sigma_n^2 \rangle_0,
\] (3.19)

and

\[
\delta F_2^{\text{SRO}} = -\frac{2}{kT} \sum_{\{mn\}} V_{mn}^2 c_m(1 - c_m)c_n(1 - c_n).
\] (3.20)

In case of \( V > 0 \) (exothermic alloying), consecutive terms in the untruncated expansion (Eq. (3.18)) have alternating signs, and depending on the value of the \( V/kT \) parameter and on the crystal structure, the convergence can be sluggish [81]. Therefore, for the truncated series a better approximation is to use summation by arithmetic means [82], namely to calculate \( \delta F_2^{\text{SRO}} = (\delta F_1^{\text{SRO}} + \delta F_2^{\text{SRO}}) / 2 = \delta F_2^{\text{SRO}} / 2 \) instead of \( \delta F_2^{\text{SRO}} \).

### 3.4.2.2. The free energy concentration expansion (FCEM)

In case of dilute solid-solution a partial summation of the cumulant series (3.18) becomes possible. This can be achieved by rearranging the power series in inverse-temperature into a power series in concentration. According to Eqs. (3.16) and (3.17) the contribution of SRO effects to the alloy free energy is given by:

\[
\delta F^{\text{SRO}} = -kT \ln \left[ 1 + \sum_{s=1}^{\infty} \frac{1}{s!} \left( -\frac{1}{2kT} \right)^s \left\langle \left( \sum_{\{mn\}} V_{mn} \Delta \sigma_m \Delta \sigma_n \right)^s \right\rangle_0 \right].
\] (3.21)

This expression is symmetric with respect to \( A \leftrightarrow B \) exchange, because while \( \Delta \sigma_m \) changes sign, \( \Delta \sigma_m \Delta \sigma_n \) does not. Therefore, the most suitable concentration-related expansion parameter seems to be \( u_m = c_m(1 - c_m) \).
Since $\langle \Delta \sigma_m \rangle_0 = 0$, and as can be shown for $s \geq 2$ (with contributions linear with respect to $u$)

$$
\langle (\Delta \sigma_m)^s \rangle_0 = 2^s u_m + O(u_m^2),
$$

(3.22)

Eq. (3.21) can be presented as

$$
\delta F^\text{SRO} = -kT \ln \left( 1 + \sum_{s=2}^{\infty} \frac{1}{s!} \left( -\frac{1}{2kT} \right)^s \sum_{\{mn\}} V_{mn}^s 2^{2s} u_m u_n \right),
$$

which is exact with respect to $u_m u_n$ (“second-order” approximation).

Changing the order of summation and expansion of the logarithmic function gives the SRO correction,

$$
\delta F^\text{SRO} = -kT \sum_{\{mn\}} c_m (1-c_m) c_n (1-c_n) \left( \exp \left( -\frac{2V_{mn}}{kT} \right) + \frac{2V_{mn}}{kT} - 1 \right).
$$

(3.23)

Together with (3.10) it gives the following expression for the free energy of the alloy,

$$
F = kT \sum_p N_p \left( c_p \ln c_p + (1-c_p) \ln (1-c_p) \right) + \sum_p N_p H_p (2c_p - 1)
+ \sum_{\{mn\}} \left( \frac{1}{2} V_{mn} (2c_m - 1)(2c_n - 1) - kT c_m (1-c_m) c_n (1-c_n) \left( \exp \left( -\frac{2V_{mn}}{kT} \right) + \frac{2V_{mn}}{kT} - 1 \right) \right).
$$

(3.24)

While it is absolutely accurate in the dilute limit, for other concentrations higher-order contributions of the expansion should be taken into account. The high accuracy of the SRO correction derived by means of FCEM was confirmed by comparison of calculated segregation levels with results of Monte-Carlo simulations (see Section 5.3) [20,83].

3.5. The segregation equations

Given appropriate expressions for the free energy of a semi-infinite solid-solution, such as the SRO–FCEM formula (Eq. (3.24)), there are two approaches for getting the layer compositions. In one procedure, imposing the bulk composition at some depth, segregation profiles can be calculated by means of direct numerical minimization of the free energy with respect to the concentrations of a finite number of near-surface layers. Alternatively, a set of coupled equilibrium equations in composition can be obtained analytically by minimization of the free energy expression ($\partial F / \partial c_p = 0$). They have the same exponential form as the Langmuir–McLean Eq. (3.2), but the segregation profile extends from the top surface layer ($p = 0$) down to the bulk (with concentration $c$), and interactions–correlations effects are included,

$$
\frac{c_p}{1-c_p} = \frac{c}{1-c} \exp \left( -\frac{\Delta T^{\text{BW}}_p + \Delta F^{\text{SRO}}_p}{kT} \right).
$$

(3.25)

For the case of first-neighbor interactions, the segregation energy in the BW approximation ($\Delta F^{\text{SRO}}_p = 0$) reads
\[ \Delta U_{p}^{BW} = \Delta h_p + \Delta H_{p}^{em} + \sum_{q} Vz_{pq}(2c_{q} - 1) - Vz(2c - 1), \]  

(3.26)

where the bulk coordination number is denoted by \( z \), and \( z_{pq} \) is the coordination number of a \( p \)-plane atom with respect to neighboring \( q \)-plane atoms. This approach corresponds to the regular solution model with \( V = -\Delta E_m/(zc^2_{1}c^2_{2}) \). Hence, if nearest-neighbor sites are in nearest-neighbor planes only and assuming \( \Delta h_0 = (\gamma_A - \gamma_B)\lambda_0 \), Eq. (3.26) for \( \Delta U_{0}^{BW} \) coincides with (3.3).

Taking into account the SRO correction to the BW free energy by means of the free-energy expansions (Section 3.4.2), the corresponding correction term to the (multilayer) excess segregation free energy reads

\[ \Delta F_{p}^{SRO} = \sum_{q} f(V)z_{pq}c_{q}(1 - c_{q})(2c_{p} - 1) - f(V)zc(1 - c)(2c - 1), \]  

(3.27)

with \( f(V) \) depending on the specific correlational approximation used, namely,

\[ f(V) = \frac{2V^2}{kT}, \]  

(3.28)

for the \( \Delta F_{2}^{SRO} \) approximation,

\[ f(V) = \frac{V^2}{kT}; \]  

(3.29)

for the \( \Delta F_{2}^{SRO} \) approximation, and

\[ f(V) = kT \left[ \exp \left( -\frac{2V}{kT} \right) + \frac{2V}{kT} - 1 \right], \]  

(3.30)

in the free energy concentration expansion (FCEM) approximation.

The effective pair interactions at an alloy surface could be enhanced [58] or reduced [84] relative to the bulk value, and then \( V \) should be replaced by \( V_0 \) in terms corresponding to \( p \) or \( q = 0 \) in Eqs. (3.26) and (3.27). Although the equations have been written explicitly for the case of nearest-neighbor interactions, they can be easily generalized by additional summations over interactions in several coordination spheres.

The set of coupled equilibrium equations can be solved consecutively by a trial-and-error iterative procedure starting with a guessed \( c_0 \) value for the concentration in the top layer and assuming bulk concentration at a certain depth underneath (for example, see Section 5.2).

Area-preserve mapping. This is an attractive mathematical tool for describing segregation profiles demonstrated for Pt–Ni alloys within the BW approximation [54,85], including the reproduction of the face-related segregation reversal observed for (111) vs. (110) face [86]. In case each atom in a \( p \)-layer has nearest neighbors in the three \( p - 1 \), \( p \) and \( p + 1 \) layers only, the layer concentrations or enrichment factors, \( \alpha_p = c_p/c - 1 \) are coupled (in Eq. (3.25)) in the following general form:

\[ \alpha_1 = g_1(\alpha_0), \quad \alpha_2 = g_2(\alpha_0, \alpha_1), \quad \alpha_{p+1} = g(\alpha_{p-1}, \alpha_p), \ldots, \]  

(3.31)

or with a two-dimensional transformation,

\[ \begin{pmatrix} \alpha_{p-1} \\ \alpha_p \\ \alpha_{p+1} \end{pmatrix} \rightarrow \begin{pmatrix} \alpha_p \\ \alpha_{p+1} \end{pmatrix}. \]  

(3.32)
Linearization of the transformation for large $p$ and small $\varphi_p$ in a solid-solution allows the application of “area-preserving map” [54,85],

$$
\begin{pmatrix}
\varphi_p \\
\varphi_{p+1}
\end{pmatrix} = C
\begin{pmatrix}
\varphi_{p-1} \\
\varphi_p
\end{pmatrix},
$$

(3.33)

with a unitary transformation matrix $C$. Its eigenvalues, $\lambda = \varphi_{p+1}/\varphi_p$, characterize the decay in depth of the segregation concentration profile.

The method can be applied both in the BW and in the free-energy expansion approximations, and it eliminates possible convergence problems in the trail-and-error procedure for solving the segregation equations [54]. For example, according to the linearized Eqs. (3.25), (3.26) and (3.27), for the (100)-planes in f.c.c. solid-solutions

$$
C = \begin{pmatrix}
0 & 1 \\
-1 & -r
\end{pmatrix},
\quad r = \frac{2V + kT/4c(1-c) + f(V)[10c(1-c) - 1]}{2V + f(V)[4c(1-c) - 1]},
$$

(3.34)

and $f(V)$ is given by Eqs. (3.28)–(3.30). (The BW-type approximation corresponds to $f(V) = 0$).

The eigenvalues of the matrix $C$ read,

$$
\lambda = -\frac{r}{2} \pm \sqrt{\frac{r^2}{4} - 1},
$$

where the plus sign holds for ordering alloys ($V > 0$) with oscillatory in-depth profile, while for phase-separating alloys ($V < 0$) $\lambda$ is positive and the profile is monotonous. As calculated by us (Fig. 5), absolute values of $\lambda$ in the FCEM approximation are smaller than in the BW approximation, so that the concentration profile is more damped. Other effects of SRO on segregation are discussed in detail in Section 5.

![Fig. 5. Calculated SRO effects on segregation profile damping: relative enrichment in consecutive atomic layers ($\lambda$) vs. reduced temperature for f.c.c. solid-solution (bulk concentration $c = 0.09$) in the free energy concentration expansion (FCEM) (solid line) compared to the BW approximation (dotted line). When $|\lambda|$ is smaller, the segregation profile is shallower.](image-url)
3.6. Discussion of some thermodynamical aspects

Even without relating to any particular model of the alloy free energy, general equilibrium equations can be derived just from the thermodynamic law of free energy minimum, while taking into account the conservation of the total number of constituent atoms in the alloy, namely, \( N \sum_p (c_p - c) = 0 \) (\( N \) is the number of sites per each layer). Using the Lagrangian multiplier technique, one obtains the following condition for the free-energy minimum:

\[
\frac{\partial}{\partial c_p} \left[ F - \mu N_1 \sum_p (c_p - c_b) \right] = 0 \quad \text{for all} \quad p.
\]  

(3.35)

According to this equation, the “\( p \)-layer chemical potential”,

\[
\mu_p = \frac{1}{N_1} \frac{\partial F}{\partial c_p},
\]

(3.36)
equals the Lagrangian multiplier \( \mu \). Thus, \( \mu_p \) does not depend on \( p \) [87, 88] and coincides at equilibrium with the bulk chemical potential,

\[
\mu_p = \mu, \quad \text{or} \quad \frac{\partial F}{\partial c_p} = \frac{\partial F}{\partial c}.
\]

(3.37)

Variation in a function (\( Y \)) of the alloy state, related to segregation of atom A from the bulk (b) to a near-surface \( p \)-layer can be written as,

\[
\Delta Y_p = Y(\ldots, N_p^{(A)} + 1, \ldots, N_b^{(A)}, \ldots) - Y(\ldots, N_p^{(A)}, \ldots, N_b^{(A)} + 1, \ldots)
\]

\[
= \left[ Y(\ldots, N_p^{(A)} + 1, \ldots, N_b^{(A)}, \ldots) - Y(\ldots, N_p^{(A)}, \ldots, N_b^{(A)} + 1, \ldots) \right]
\]

\[
+ \left[ Y(\ldots, N_p^{(A)}, \ldots, N_b^{(A)} + 1, \ldots) - Y(\ldots, N_p^{(A)}, \ldots, N_b^{(A)}, \ldots) \right]
\]

\[
= \frac{\partial Y}{\partial N_p^{(A)}} - \frac{\partial Y}{\partial N_b^{(A)}} = \frac{1}{N_1} \left( \frac{\partial Y}{\partial c_p} - \frac{\partial Y}{\partial c} \right). \quad (3.38)
\]

From Eq. (3.37) follows that the segregation related variation of the alloy free-energy is 0 at equilibrium:

\[
\Delta F_p = \frac{1}{N_1} \left( \frac{\partial F}{\partial c_p} - \frac{\partial F}{\partial c} \right) = \mu_p - \mu = 0
\]

(3.39)

(or as expected for a reversible process, \( \Delta U_p = T \Delta S_p \)).

The energy, entropy and the free-energy of an ideal solid-solution are equal to \( U^{id} = 0 \), \( S^{id} = S^{BW} \) and \( F^{id} = -TS^{BW} \) (Section 3.3), respectively, so “excess” free-energy can be defined as,

\[
F^{ex} = F - F^{id} = U - TS^{ex},
\]

(3.40)

where the excess entropy is \( S^{ex} = S - S^{BW} \).

From (3.37) and (3.40) it follows that

\[
\frac{\partial S^{BW}}{\partial c_p} - \frac{\partial S^{BW}}{\partial c} = \frac{1}{T} \left( \frac{\partial F^{ex}}{\partial c_p} - \frac{\partial F^{ex}}{\partial c} \right).
\]

(3.41)
Using Eqs. (3.8) and (3.38) gives the same form of equilibrium multilayer segregation equations as the Langmuir–McLean Eq. (3.2) or the (3.25) system,

\[
\frac{c_p}{1 - c_p} = \frac{c}{1 - c} \exp \left[ - \frac{1}{kT} \left( \frac{\partial F_{\text{ex}}}{\partial c_p} - \frac{\partial F_{\text{ex}}}{\partial c} \right) \right] = \frac{c}{1 - c} \exp \left[ - \frac{\Delta F_{p}^{\text{ex}}}{kT} \right].
\] (3.42)

Its application requires adequate estimations of the excess free-energy of segregation, \(\Delta F_{p}^{\text{ex}}\), including (in addition to \(\Delta U_{p}^{\text{BW}}\)) contributions of SRO, vibrations, etc.

Starting from some (negative) non-equilibrium free-energy change with respect to the bulk-truncated non-segregated state, it varies with the surroundings of \(p\)-layer atoms as the segregation proceeds to equilibrium (for which \(\Delta F_{p} = 0\)). The “average” free-energy change, \(\bar{\Delta F}_{p}\) (over all atoms segregated in the process), should be negative. \(\bar{\Delta U}_{p}\) and \(\bar{\Delta S}_{p}\) usually do not coincide with \(\Delta U_{p}\) and \(\Delta S_{p}\), and obey

\[
\bar{\Delta U}_{p} - T\bar{\Delta S}_{p} = \Delta F_{p}.
\] (3.43)

(In contrast to changes in energy and entropy at equilibrium, their average values can have opposite signs at some temperature interval.)

It should be noted that usually (and in analogy to adsorption from the gaseous phase) surface segregation in solid-solutions is exothermic, and the segregation level decreases with temperature, in accordance with the Le Chatelier principle. While this process is accompanied by a decrease in entropy, the entropy of sufficiently ordered alloys can increase in a process of energetically unfavorable segregation-related disordering. Therefore, in spite of possible surface tension or size-mismatch driving forces for segregation, the “reaction” can be endothermic and enhancement of segregation with temperature should occur. Since order is diminished with increasing temperature, the reaction can eventually become exothermic and the surface concentration of the segregant starts to decrease. A maximum in the segregation equilibrium level can thus, be expected at a temperature region corresponding to \(\Delta U_{p} = \Delta S_{p} = 0\), close to the bulk order–disorder transition. Fig. 6 summarizes schematically the anticipated complete temperature dependence of surface segregation in alloys with

![Fig. 6. Schematics of the evolution of equilibrium segregation with temperature in alloys with order-segregation competition: (a) dominant surface segregation tendency; (b) dominant ordering tendency.](image-url)
order/segregation competition. It should be noted that the *peaked* segregation curve for the case of dominant ordering tendency (b) is quite unfamiliar, and some examples of entropy-driven segregation in ordered alloys that increases with temperature will be presented in Section 4.

In a solid-solution the relationship between the segregation curve slope and the thermal nature of the process can be verified by applying relationships (3.36–3.38), and $S = -\partial F / \partial T$,

$$\Delta U_p = T \Delta S_p = TN_l \sum_q \Delta(\mu_q)p \frac{\partial c_q}{\partial T}. \quad (3.44)$$

Since at the temperature of maximal segregation, $\partial c_q / \partial T = 0$ for all $q$ (assuming the same temperature for all layers, although these temperatures can slightly differ), $\Delta U_p = 0$, and the segregation reaction is non-thermal. Rearranging (3.44) gives the slope of the monolayer segregation vs. $T$ curve,

$$\frac{\partial c_0}{\partial T} = \frac{\Delta U_0}{TN_l \Delta(\mu_0)_0}. \quad (3.45)$$

During the segregation process the surface chemical potential increases upon approaching the bulk value $\Delta(\mu_0)_0 > 0$, so according to this equation the slope of the segregation plot has the same sign as the energy of the segregation, namely, it is positive (negative) for endothermic (exothermic) segregation.

When a maximal segregation level occurs in the solid-solution region (see Section 5.2), the non-negligible correction (excess) to the BW value of the segregation entropy, $\Delta S_0^\text{ex}$ (associated with SRO, for example), can be easily calculated from measured $c_0^{\text{max}}$ using Eq. (3.42)

$$\Delta S_0^\text{ex} = k \ln \frac{c_0^{\text{max}} (1 - c)}{c (1 - c_0)}, \quad (3.46)$$

which equals $-\Delta S_0^\text{BW}$ (for non-thermal segregation $\Delta S_0 = \Delta S_0^\text{BW} + \Delta S_0^\text{ex} = 0$). Otherwise, $\Delta S_0^\text{ex}$ and $\Delta U_0$ in a certain temperature region, can be determined from the intercept and slope of the experimental $k \ln[c_0(1-c)/c(1-c_0)]$ vs. $1/T$ plot.

In order to compare segregation energies and excess entropies in different alloys or for different surface orientations of the same alloy, the following form of the equilibrium equation can be used,

$$\Delta U_0 = T \Delta S_0^\text{ex} - kT \ln \frac{c_0(1-c)}{c(1-c_0)}. \quad (3.47)$$

If $\Delta S_0^\text{ex}$ varies much stronger than $\Delta S_0^\text{BW}$ at some “compensation” temperature, corresponding to close values of the surface concentrations, a linear relationship between the excess entropy and energy of segregation should exist [89]. Indeed, a linear dependence was revealed by Monte-Carlo calculations for Pd segregation in Ni at a number of interfaces [90], and by Si, P and C segregation determined experimentally for different grain boundaries in $\alpha$-iron, as is shown in Fig. 7 [90,91].

### 3.7. Monte-Carlo simulations

Monte-Carlo (MC) stochastic computer simulations represent a powerful non-analytical approach to study of surface phenomena [93]. Briefly, by using (pseudo-) random numbers, a succession of atomic

---

1 The same thermodynamical theory (with different energetics) is applicable also to segregation at grain boundaries or other interfaces.
configurations is produced with probabilities constructed according to a specific (canonical or grand canonical) statistical-mechanical ensemble. The true distribution function is obtained independently of the initial state, after a sufficient number of steps, by means of proper quantification of one step probabilities for transition between configurations. Then, alloy properties can be calculated as averages over the generated configurations.

The MC approach facilitates the estimation of SRO at the surface [27], as well as effects of atomic vibrations and surface relaxation [28,29], which are difficult to evaluate analytically. One of the advantages of the MC approach is that it can go beyond both the BW approximation and the Ising model and applied in the frameworks of various models for the alloy energy:

- Constant bond energies [94], including effective Ising Hamiltonian derived from electronic structure of the disordered alloy in the tight-binding Ising model (TBIM) [58,63]. In particular, the latter was used in study of the (111) surface of Cu–Ag alloys [30];
- Lennard-Jones potential [21] or other empirical interatomic potentials [26];
- $N$-body potential designed on the basis of bulk energetics and mechanical properties as used recently in a Monte-Carlo study of the thermal properties of Cu$_3$Au low index surfaces [32];
- The embedded atom method (EAM), based on approximate, but rather realistic considerations about atomic energies and interactions in an alloy [22–25]. In this method the energy of a configuration is computed as:

$$E = \sum_i F_i(\rho_i) + \frac{1}{2} \sum_{ij, i \neq j} \phi_{ij},$$

where $F_i(\rho_i)$ is the energy (usually negative) involved in embedding atom $i$ into the local electron density, $\rho_i$, due to the remaining atoms, approximated by the superposition of atomic densities. Positive $\phi_{ij}$ stands for screened internuclear repulsion between cores for atoms $i$ and $j$. In the EAM
the local environment of an atom affects its interactions with neighbors, so that the lattice strain
energy and its possible relaxation upon surface segregation or reconstruction are implicit in the
formalism. Applications of EAM–MC in surface segregation of several alloy systems, including SRO
effects, were reported by Foiles [24].
- Representation of alloy energy as a sum of the energies of individual atoms according to the
  semi-empirical BSF method developed by Bozzolo et al. [95]. This method [95], based on ideas
  of equivalent crystal theory [96] for defect formation in elemental solids, allows to study surface
  structure including relaxation for atoms of different species. In particular, it was applied in
  Monte-Carlo calculations of the heat of segregation of single substitutional impurities in f.c.c.
  metals [31].

It should be noted that in spite of the above mentioned advantages of the Monte-Carlo simulations,
they have also drawbacks such as the absence of analytical equations allowing to express one physical
characteristic of the system via others. Furthermore, they demand much more computer time compared
to analytical approaches, especially for calculation of several physical characteristics, such as the free-
energy or the chemical potential.

4. Surface segregation in ordered alloys: calculated and experimental results

Among the characteristics of ordered-alloy surfaces, one can distinguish between the low or
intermediate temperature state (the energetically favorable shallow termination), its evolution with
temperature and, at even higher temperatures, the occurrence of distinct order–disorder surface phase
transitions (Section 6). Experimental determination of equilibrium terminations at low temperatures can
be hampered by kinetic limitations.

4.1. The surface stable termination and its evolution with temperature in b.c.c.- and f.c.c.-based alloys

Spatial ordering in the bulk of alloys and “classical” surface segregation in completely random solid-
solutions (without LRO or SRO) are both exothermic processes, which are enhanced at lower
temperatures and accompanied by a decrease of the configurational entropy. As discussed in Section
3.6, the interplay of segregation and ordering in ordered alloys can result either in endothermic or
exothermic segregation, depending primarily on the energy balance of near-surface broken bonds. In
the former case an increase in equilibrium segregation levels with temperature can be expected due to
the predominant enhancement of compositional disorder that disrupts the near-surface LRO, and is
associated with increased configurational entropy. It should be noted that endothermic segregation can
occur, in principle, also at temperatures higher than the order–disorder transition, namely, in solid-
solutions with considerable SRO, as will be shown in Section 5. Still, at sufficiently high temperatures
ordering effects are relatively weak and the segregation level always decreases with temperature.

The competition between ordering tendencies and surface segregation was predicted first by Monte-
Carlo calculations [94], and later by the BW approximation [10,11]. Its occurrence was demonstrated
also by several theoretical studies which went beyond the BW approximation [12,13]. In particular, the
cluster variation method (CVM) was applied to the AB b.c.c.(110) ordering alloys (B2 structure) on the
basis of a model of pair-wise interactions between nearest-neighbor atoms [12]. Depending on the ratio
of the basic segregation driving force to the effective interatomic interactions ("alloying parameter"),

\[ \Delta = \frac{V_{AA} - V_{BB}}{V_{AA} + V_{BB} - 2V_{AB}}, \]  

(4.1)

the following behavior was predicted (Fig. 8):

---

Fig. 8. The competition between segregation and order: surface concentration (a), bulk and surface LRO and SRO parameters (b), defined in Section 2.2, as function of the reduced temperature $kT/W$ ($W=2V$) for the (110) face of $AB$ b.c.c. alloy for various values of the energetic parameter $\Delta$, defined in the text [12]. The low temperature segregation changes from endothermic to exothermic with increasing $\Delta (>3)$, and the segregation maximum ("non-thermal" segregation) in the former case corresponds to the order–disorder transition temperature, $T_c$. 
(i) The case of relatively weak segregation ($\Delta < 3$ for this structure). Starting at $T = 0$ with stoichiometric perfect “bulk truncated order” (BTO) at the outermost layer, the surface concentration increases with heating, up to a maximal value at the phase transition temperature, followed by desegregation at higher temperatures (a peaked segregation vs. temperature curve, Fig. 8a, as in Fig. 6b);

(ii) The case of relatively strong segregation ($\Delta > 3$). The order is disrupted by pure element segregation at $T = 0$, followed by desegregation at higher temperatures (a monotonously decreasing “Langmuir–McLean-type” temperature dependence, Fig. 6a).

In case (i) a relatively strong tendency for ordering impedes segregation that grows with temperature in endothermic “segregation reaction”, concurrently with a monotonous decrease of the pertinent LRO and SRO parameters (Fig. 8b). An opposite situation is expected in case (ii) where the impeded order grows with temperature and reaches a maximum.

Increase in Au concentration with temperature at the (100) surface of CuAu ($L1_0$ structure), as calculated in the tetrahedron approximation of the CVM, was explained by means of progressive decrease of the LRO (case i) [13]. Although surfaces of a considerable number of b.c.c.- and f.c.c.-based ordered alloys have been studied to date [7], there are only few examples of experimentally determined temperature dependence of the surface composition, some of which indicate endothermic segregation. Si segregating at grain-boundaries in Fe–12.9%Si [97] (Fig. 9), the Al segregation at surfaces of Ni–10%Al [35,98] and at Ni–48%Al [99] were tentatively explained by means of LRO effects. Local disorder observed near the grain-boundaries in Ni$_3$Al [100,101] can be a result of endothermic entropy-driven interfacial segregation. The next three examples clearly demonstrate that LRO can impede changes in surface composition. Fig. 10 shows the peaked segregation curve measured for Al at NiAl(100) by LEISS [102,103]. Bulk terminated order with mixed first plane (BTO$_M$) was observed at low temperatures in the extensively studied Cu$_3$Au(100) surface. A weak segregation increase with temperature (Fig. 11a [104]), or almost unchanged surface composition (Fig. 11b [105]), was observed below the bulk phase transition temperature. In case of Au$_3$Cu(100), the first layer...
consists only of Au atoms and the second layer of Cu atoms (no bulk terminated order, NBT), and, again, desegregation starts only above the bulk order–disorder transition temperature (Fig. 12 [106]).

The segregation tendency can control which of several possible surface terminations of ordered bulk (BTO) is the most stable at low or intermediate temperatures. According to results of the CVM tetrahedron approximation for the (100) surface of the f.c.c. \( L1_2 \) lattice [14–16], the termination, either pure (BTOP) or mixed (BTO\(_M\)), is primarily determined by the “surface field” \( H_0 \) in the Ising model Hamiltonian, Eq. (3.6). For example, BTO\(_M\) termination was predicted for Cu\(_3\)Au(100) [13] (in agreement with the experimental finding mentioned above [104,105]).

The ordered alloy termination at low-temperatures, governed by the interplay of ordering and segregation tendencies, can be divided into several groups and subgroups (Fig. 13):

1. Pure element termination
   1.1. with bulk truncated order (BTOP);
   1.2. without bulk truncated order (NBT\(_P\)).
2. Stoichiometric termination corresponding to bulk truncated order (BTO\(_S\))
3. Mixed surface layer termination
   3.2. with bulk truncated order (BTO\(_M\));
   3.3. without bulk truncated order (NBT\(_M\)).

Pure element surface termination that differs from any underlayer and disrupts the bulk order occurs in case 1.2 due to strong segregation tendency, whereas strong ordering tendency can result in a bulk-like termination with no segregation (case 2). Furthermore, the appearance of a mixed surface layer above pure element underlayer, or vise versa, should be determined by the relative surface energies of the two elements. Deviations from a bulk-like termination (namely, NBT\(_P\) or NBT\(_M\)) can involve surface reconstruction or temperature dependent transitions between different types of surface order as revealed by several experimental studies (e.g., Fig. 10). Thus, two ideal BTO terminations (BTO\(_P\) or

Fig. 10. Variation of the Ni/Al LEISS intensity ratio with temperature measured for NiAl(100) [103]. Surface reconstructions are indicated.
Fig. 11. Compositions of the first and second layers of Cu$_3$Au(100) as function of annealing temperature. Bulk truncated order was found at low temperatures, and first layer weak segregation increase (a) [104], or almost unchanged surface composition (b) [105], at temperatures up to $T_c \approx 663$ K (at the lowest temperatures a problem of adequate equilibration might exist).
Fig. 12. Cu concentration in the first (a) and second layer (b) of Au$_3$Cu(100) as function of annealing temperature as obtained by LEIS [106]. Desegregation starts above the bulk order–disorder transition temperature $T_c \approx 472$ K (solid line — a fit to a Langmuir–McLean type equation with the second-layer concentration used instead of the bulk value).
BTO are possible for the $L1_2(110)$ surface, but in Cu$_3$Au the reconstructed $(110)-(4 \times 1)$ structure is the most stable (Fig. 14), as determined by quantitative LEED [107]. For the $L1_2(111)$ orientation, only a single bulk-like ideal termination is expected (Section 2.2), but according to LEIS, AES and LEED measurements [108] annealing of sputtered Pt$_3$Sn(111) leads to Sn-enriched $\sqrt{3} \times \sqrt{3}R30^\circ$ reconstruction (Fig. 15a), which gradually transforms at higher temperatures to the bulk-truncated $(2 \times 2)$ structure (Fig. 15b). At still higher temperatures, it transforms to a PtSn segregated $(2 \times 2)'$ new structure (Fig. 15c).

A comprehensive compilation of experimental data regarding surface terminations of bulk ordered alloys is given in Table 1. In most of these cases the termination is governed by the tendency to lower the alloy surface tension. However, there are several deviations from this trend, corresponding mostly to

![Diagram showing binary alloy possible terminations](image_url)
constituents with similar surface tensions. Furthermore, in NiAl(111), for example, a pure Ni termination was found in spite of significantly lower surface tension of Al [109], whereas other studies [110] reported on equal amounts of Ni and Al terminated domains on this surface (no segregation on the average). This behavior of the strongly ordered NiAl alloy was explained by the relatively small value of the $D$ parameter ($\approx 1$), estimated using results of electron density functional calculations [111]. Consistently with this trend, impeded Al surface segregation was found for the solid-solution region of the Ni–Al bulk phase diagram and attributed to strong SRO effects (see Section 5.2 and [19]). Another possible factor affecting the alloy termination is the relative atomic size of the components, which can lead also to surface rippling found in LEED experiments for NiAl(110) [112], and calculated by EAM [113].

The BFS method [95] revealed that the surface energy is the lowest for the mixed composition truncation of the low-index rippled faces in the $L1_2$ structures Ni$_3$Al and Cu$_3$Au [114], in agreement with EAM calculations [115,116] and experiment (cases 2 and 3 above; Table 1).

The TBIM approach together with the BW approximation [117] were applied to study the relationship between surface segregation and the stable termination on the CuPt alloy with the $L1_1$...
ordered structure (Fig. 16). Since Cu in CuPt has a tendency to segregate, the most stable among the three possible terminations of the (111) face is the more Cu enriched termination (a) (BTO P), in agreement with experiment (Table 1). In case of CuPt(100), for the single termination possible some Cu enrichment was predicted [117].

4.2. Segregation in size-factor intermetallics

The structure of “size-factor” intermetallics is characteristic to a certain, considerable atomic size ratio of the two atomic constituents, which is less extreme than in interstitial phases. For example, when the ratio of atomic diameters equals approximately to 1.2, Laves phases, which posses a narrow range...

<table>
<thead>
<tr>
<th>Structure</th>
<th>Alloy ($\gamma_A/\gamma_B$)</th>
<th>Orientation</th>
<th>Surface termination</th>
<th>Temperature range (K)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$L_{12}$</td>
<td>Au$_3$Cu (1140,1360)</td>
<td>(100)$^b$</td>
<td>NBT$_P$ P(Au)/P(Cu)</td>
<td>&lt; 550</td>
<td>[106]</td>
</tr>
<tr>
<td></td>
<td>Au$_3$Pd (1140,1500)</td>
<td>(100)$^b$</td>
<td>BTO$_P$ P(Au)/M</td>
<td>&lt; 1123 ($T_c$)</td>
<td>[118]</td>
</tr>
<tr>
<td></td>
<td>Cu$_3$Au (1360,1140)</td>
<td>(100)$^b$</td>
<td>BTO$_M$ M/P(Cu)</td>
<td>&lt; 673</td>
<td>[105,119]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(110)$^b$</td>
<td>NBT$_M$ reconstructed (4 x 1)/25%Au/P(Cu)</td>
<td>660 → 300</td>
<td>[107]</td>
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<td></td>
<td></td>
<td></td>
<td>BTO$_S$</td>
<td>~ 370–670</td>
<td>[120–123]</td>
</tr>
<tr>
<td></td>
<td>Cu$<em>{30}$Pd$</em>{15}$ (1360, 1500)</td>
<td>(110)$^b$</td>
<td>Nearly BTO$_P$ P(89%Cu)/M(60%Cu)</td>
<td>~ 600</td>
<td>[124–127]</td>
</tr>
<tr>
<td></td>
<td>Cu$_3$Pt (1360,1800)</td>
<td>(100)$^b$</td>
<td>BTO$_P$ P(Cu)/M</td>
<td>&lt; 850</td>
<td>[128]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(110)$^b$</td>
<td>NBT$_M$ M(18%Pt)/P(Cu)</td>
<td>&lt; 800</td>
<td>[129]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(111)$^a$</td>
<td>BTO$_S$</td>
<td>~ 50–400</td>
<td>[130]</td>
</tr>
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<td></td>
<td>Ni$_3$Al (1778,914)</td>
<td>(100)$^b$</td>
<td>BTO$_M$ M/P(Ni)</td>
<td>823–1073</td>
<td>[39,131–133]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(110)$^b$</td>
<td>BTO$_M$ M/P(Ni)</td>
<td>973</td>
<td>[41]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(111)$^a$</td>
<td>BTO$_S$</td>
<td>300–1000</td>
<td>[40,134]</td>
</tr>
<tr>
<td></td>
<td>Pt$_3$Co (1800,1873)</td>
<td>(100)$^b$</td>
<td>BTO$_M$ M/P(Pt)</td>
<td>800</td>
<td>[135]</td>
</tr>
<tr>
<td></td>
<td>Pt$<em>3$Fe$</em>{0.2}$ (1800,1872)</td>
<td>(111)$^a$</td>
<td>NBT$_P$ P(Pt)/2nd, 3rd Pt-rich</td>
<td>600–1200</td>
<td>[56,136]</td>
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<td>Pt$_3$Sn (1800,544)</td>
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<td>BTO$_M$ M/P(Pt)</td>
<td>1023–1100</td>
<td>[137,138]</td>
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<td>(111)$^a$</td>
<td>BTO$_S$ at 1100, reconstructed (2 x 2)* at higher temperature</td>
<td>&gt; 1100</td>
<td>[108,137,138]</td>
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<td></td>
<td>Pt$_3$Ti (1800,1650)</td>
<td>(100)$^b$</td>
<td>BTO$_P$ P(Pt)/M</td>
<td>1000</td>
<td>[139]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(111)$^a$</td>
<td>NBT$_P$ P(Pt), other layers bulk composition</td>
<td>1100</td>
<td>[140,141]</td>
</tr>
<tr>
<td>$B_2$</td>
<td>FeAl (1872,914)</td>
<td>(100)$^b$</td>
<td>NBT$_P$ P(Al)/20%Al</td>
<td>973</td>
<td>[142–144]</td>
</tr>
<tr>
<td></td>
<td>NiAl (1778,914)</td>
<td>(100)$^b$</td>
<td>NBT$_M$ M(76%Al)/P(Ni)</td>
<td>1000</td>
<td>[102,145]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(110)$^a$</td>
<td>BTO$_S$</td>
<td>&gt; 1000</td>
<td>[112,145]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(111)$^b$</td>
<td>BTO$_P$ P(Ni)/P(Al); mixture of Ni and Al terminated domains</td>
<td>1075–1425</td>
<td>[109,110]</td>
</tr>
<tr>
<td>$D_0_3$</td>
<td>Fe$<em>{71}$Al$</em>{29}$ (1872,914)</td>
<td>(110)$^a$</td>
<td>NBT$_P$ P(Al)</td>
<td>&gt; 700</td>
<td>[146,147]</td>
</tr>
<tr>
<td>$L_{11}$</td>
<td>CuPt (1360,1800)</td>
<td>(111)$^c$</td>
<td>BTO$_P$ P(Cu)</td>
<td>600</td>
<td>[117]</td>
</tr>
</tbody>
</table>

$^a$ A single surface termination of the bulk order is possible (f.c.c.-based $L_{12}(111)$, and b.c.c.-based $B_2(110)$ and $D_0_3(110)$).

$^b$ Two surface terminations of the bulk order are possible ($L_{12}(100)$, $L_{12}(110)$ and $B_2(100)$).

$^c$ Three surface terminations of the bulk order are possible (f.c.c.-based $L_{1_1}$).

Table 1
Experimentially determined surface terminations of ordered binary alloys (M/P: mixed surface layer above pure element underlayer, P/M: pure element surface above mixed underlayer, P/P: (nearly) pure element surface layer above pure underlayer, $\gamma(T_m)$: surface tension (mN/m) of the pure element liquid metal at its melting points (in K)).
of homogeneity and stoichiometric composition, are formed [4]. Their bulk thermal disordering is prevented almost to the melting point due to the relatively high energetic barrier for penetration of the larger atoms into the smaller atom sites (“antisites”). Moreover, as demonstrated recently for MgNi$_2$, such geometrical factors can play a role in surface segregation phenomena as well, when size-related energy differences (Section 3.2) between near-surface sites of the larger atom and surface antisites should be significantly lower than for the bulk antisites (Fig. 17) due to the reduced coordination and possible surface relaxation or reconstruction. The corresponding site–antisite atomic exchange process can be further facilitated due to surface tension differences of the two constituents, so that the segregation can become exothermic leading to the normal (“Langmuir–McLean”) temperature dependence. Nevertheless, significant transfer of the larger atoms from bulk sites to surface antisites is expected even in case of endothermic segregation (depicted in Fig. 17), and the entropy-driven exchange process should be enhanced with increasing thermal energy (Section 3.6). Such temperature

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**Fig. 16.** The three possible BTO type terminations of the $L_1_1$(111) face: (a) two pure layer variants, and (b) mixed termination. The single (mixed) termination of the $L_1_1$(100) face is shown in (c) [117].
dependence was observed recently for Mg segregation in MgNi$_2$ thin films [148,149] and the reported data have been analyzed on the basis of this energetic model [150], which seems to be adequate to “size-factor” intermetallics in general.

The intermetallic MgNi$_2$ compound has the ordered C36 hexagonal Laves phase structure formed by packing together Mg and Ni atoms in separate (0001) layers of a simple triangular arrangement ($T$) and a “Kagome” network of triangles and hexagons ($K$-layers in Fig. 18) [4]. In the analysis, the surface

Fig. 17. Schematics of the relative positions of energy-wells for endothermic disordering exchange processes of the larger atoms in size–factor intermetallics between their equilibrium positions (○) and a bulk antisite (●) or a surface antisite (○) [150].

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The intermetallic MgNi$_2$ compound has the ordered C36 hexagonal Laves phase structure formed by packing together Mg and Ni atoms in separate (0001) layers of a simple triangular arrangement ($T$) and a “Kagome” network of triangles and hexagons ($K$-layers in Fig. 18) [4]. In the analysis, the surface

Fig. 18. Illustration of the atomic arrangement in a Laves phase structure with larger atoms, e.g. Mg (○) and smaller atoms, e.g. Ni (●) in MgNi$_2$: (a) Side view of the (KTTTK) five layer sandwich; (b) top view of the two outermost layers used in the calculation ($K_0$ and $T_1 \sim 1.4$ Å apart) [150].
composition was calculated as function of temperature for a symmetric slab (relative to the middle layer) composed of an even number of sandwiches, \( m \), and a total odd number of layers, \( 4m + 1 \), assuming that the outermost layer is the dense, pure Ni, \( K \)-layer (Fig. 18b). The constant pair-interaction calculations were based on the Bragg–Williams approximation (3.10) with a lattice-dependent size mismatch contribution, \( \Delta H_{sm} \) (Fig. 17). In order to obtain the layer equilibrium compositions, the free-energy was minimized numerically under the constraint of conservation of overall film concentration. For comparison with the experimental data, the relative abundance of the corresponding two sites (\( K_0 : T_1 = 3:1 \)), was considered by calculating the average \( c_S = (3c_0 + c_1)/4 \), where \( c_0 \) and \( c_1 \) are the individual layer concentrations. The minimization was performed with respect to the four layer concentrations of the external sandwich and the four ones of the internal sandwiches (see Fig. 18). The mismatch energy for the outermost layer, \( \Delta H_{0}^{sm} \), was the only parameter adjusted in order to improve the agreement between the calculated and the experimental surface concentrations (Fig. 19), yielding a value of 0.32–0.38 eV, which is considerably lower than the mismatch energy of Mg dissolved in the bulk of Ni, estimated on the basis of a simple linear elasticity theory. The calculations show that the non-segregated, fully ordered termination (BTO\( P \)) in MgNi\( _2 \) is energetically preferable, so the segregation process is expected to be endothermic in this system, leading to the observed temperature dependence. The net main atomic exchange processes between shallow layers leading to Mg segregation are (Fig. 19),

\[
\text{Mg}_{(1,3)} + \text{Ni}_{(0)} \rightarrow \text{Mg}_{(0)} + \text{Ni}_{(1,3)}
\]

with the number of Mg atoms segregated to the outmost layer from the non-nearest neighbor third underlayer being somewhat larger than Mg originated from the nearest neighbor first underlayer. The role of the film thickness is discussed in Section 6.3.
5. SRO effects on surface segregation in solid-solutions

Effects of spatial correlations between neighboring atoms (see Section 2.1), have been usually ignored in theoretical calculations of surface segregation in solid-solutions, and the simplistic Langmuir–McLean Eq. (3.2) for equilibrium segregation in a binary \( AB \) solid-solution has been often applied quite successfully to the description of the temperature dependence. Few early attempts to go beyond the ordinary, non-correlational BW-type theories predicted only weak SRO effects in solid-solutions. Thus, using the quasi-chemical approximation, it was found that ordering tendency lowers somewhat the segregation level [151]. Reasons for the weakness of SRO effects in many alloys and the conditions under which they can become significant will be discussed in Section 5.2.

Since interatomic correlations play an important role in several bulk properties, especially at temperatures not much higher than the phase-transition temperature, SRO is expected, in principle, to affect surface segregation phenomena as well. Direct observation of surficial short-range order has been found, for example, in Pt segregated Ni\(_3\)Pt (111) surface by means of scanning tunneling microscopy [152], in agreement with Monte-Carlo calculations using the embedded-atom method [27] (see Fig. 2). In another study the calculated surface-related SRO parameters differed significantly from the bulk values [153,154]. Atomistic simulations of the Cu\(_3\)Au(001) surface showed that in contrast to LRO, SRO does not change significantly across the order–disorder transition [155]. The SRO in the near (001) surface region of this alloy was investigated above the critical temperature by glancing–incidence X-ray diffraction [156] and by Monte-Carlo simulations, revealing atomic configurations in the form of ordered domains and clusters in a disordered matrix (Fig. 20).

5.1. Evaluation of basic segregation trends

The explicit formulae for equilibrium segregation in solid-solution with SRO derived in Sections 3.4–3.5 can be applied quantitatively once relevant energetic parameters are available (Section 5.2). Yet, qualitative estimation of the SRO effects can be achieved by means of simple thermodynamical considerations. Such an approach does not rely on any statistical-mechanical approximation, and can help to gain insight into the possible role of SRO.

In the following, it is convenient to use individual “\( p \)-layer free-energy wells” for the dependence of the free-energy on the layer concentration. The equality \( \mu_p = \mu_b \) (Section 3.6) shows that at equilibrium the slopes of all free-energy wells vs. layer concentration should be identical. Atoms of a given constituent pass from a layer with greater chemical potential to a layer with smaller one, until this equality is achieved. Any additional “perturbation” (e.g., SRO) that changes the layer and bulk chemical potentials by the amounts \( \delta \mu_p \) and \( \delta \mu_b \), respectively, increases the layer concentration if \( \delta \mu_b > \delta \mu_p \), and reduces it in case \( \delta \mu_b < \delta \mu_p \).

As was noted in Section 3.3 (Eq. (3.11)), the overall contribution of interatomic interactions to the free-energy can be viewed as composed of two terms, the interaction effect in the BW-type approximation, and SRO related perturbation, which considers the non-randomness of the actual distribution of solute–solvent atoms in a solid-solution, as depicted in Fig. 20. While interaction effects on segregation trends in the BW approximation are well known (e.g., in a review by Sparnaay [11]), the basic physical mechanism of SRO induced segregation effects have been clarified only recently [157] by relying on the following assumptions:
1. Unlike the BW case, the SRO driving force ($\delta\mu_{\text{SRO}}$) and the correction $\delta F_{\text{SRO}}$ vanish together with SRO at the two dilute limits and at sufficiently high temperatures, as a result of weakening and disappearance of compositional fluctuations.

2. $\delta F_{\text{SRO}}$ has an extremum (minimum) at equiatomic composition, $c_A = c_B = 0.5$, due to the $A \leftrightarrow B$ exchange symmetry (see Section 3.4.2.2).

3. $\delta F_{\text{SRO}}$ is always negative, since as a result of SRO related changes in the atom local surroundings, the overall free-energy is lowered, compared to the value predicted for the completely random alloy.

These ordered micro-regions (or “compositional fluctuations”) always attract solute atoms (and repel solvent atoms), and thus, in case of demixing (mixing) tendency, clusters of like (unlike) atoms are able to grow (Fig. 21). As discussed above, this implies a decrease of the chemical potential of atomic layers composing the micro-regions, as compared with the BW value for $c < 1/2$ ($\delta\mu_{\text{SRO}} < 0$), and its increase for $c > 1/2$ ($\delta\mu_{\text{SRO}} > 0$; for $c = 1/2$ $\delta\mu_{\text{SRO}} = 0$). These assumptions enable to outline the corresponding short-range order free-energy wells given in Fig. 22. As is indicated, the BW driving forces increase or decrease the solute concentration, depending on the mixing or demixing tendency, while the SRO driving force always tends to increase the solute concentration level.

Proceeding to the issue of surface bulk equilibrium, in the present qualitative approach details of possible composition in-depth gradients are ignored, and equal interactions for the bulk and the surface...
layer are assumed. The surface free-energy well should be shallower and less steep than the bulk one, due to the reduced surface atomic coordination. Pure SRO effects on surface segregation (beyond the BW-approximation) can be qualitatively assessed by comparing the SRO driving force directions in the bulk ($\delta \mu^\text{SRO}_b$) and at the surface ($\delta \mu^\text{SRO}_0$), and their relative strength. Such a comparison has been done for specific concentration ranges by inspecting the corresponding surface and bulk SRO related wells [157]:

![Fig. 21. Illustration of short-range order effects in a binary solid-solution. Driven by interatomic forces, solute atoms are attracted to local compositional fluctuations: (a) mixing tendency, (b) demixing tendency [157].](image)

![Fig. 22. Atomic interaction contributions to a solid-solution free-energy as function of concentration: (a) Bragg–Williams approximation, (b) short-range order induced perturbations (the corresponding change in chemical-potential is given by the dashed line). Arrows denote driving force directions. [157].](image)
(i) **Dilute solid-solution.** $\delta \mu_{0}^{\text{SRO}}$ vanishes due to weak compositional fluctuations in the bulk of the dilute alloy. The stronger fluctuations at the non-dilute segregated surface lead, in principle, to segregation enhancement for $c_{0} < 1/2$ (Fig. 23a), or to its suppression for $c_{0} > 1/2$.

(ii) **Intermediate bulk concentration (non-dilute, $c > 1/2$).** Since the bulk free-energy well is steeper in this range (see Fig. 23b), the bulk SRO driving force is stronger, $|\delta \mu_{0}^{\text{SRO}}| > |\delta \mu_{0}^{\text{SRO}}|$. Consequently, the tendency to increase the bulk solute concentration suppresses solute surface segregation. In case $c_{0} > 1/2$, the surface SRO driving-force amplifies this suppression.

(iii) **Equiatomic solid-solution.** The SRO induced attraction of solute atoms to the bulk vanishes for $c = 1/2$, and so the surface SRO driving force can become dominant. Then, similarly to case (i), it can either enhance or diminish segregation levels.

This analysis assumed uniform solute–solvent interactions, whereas in transition metal alloys, for example, the interactions can be enhanced at the surface [58]. In such a case, depending on the enhancement magnitude, the bulk free-energy well can be shallower and less steep than the surface one (reversal of the corresponding graphs in Fig. 23). Therefore, instead of suppression, segregation enhancement is predicted for the intermediate composition range, case (ii). Based on these conclusions, a schematic diagram of SRO effects on surface segregation as function of bulk composition can be constructed [157]. The magnitude of the enhancement or suppression effects, as well as the exact boundaries between the corresponding regions in the diagram, can be determined only on the basis of calculations for specific binary solid-solution and surface orientation using a statistical-mechanical
approach such as the FCEM approximation (Section 3.4.2.2). Since the equilibrium condition is
\[ \mu^0_{BW} + \delta \mu^0_{SRO} = \mu_b^{BW} + \delta \mu^b_{SRO}, \]  
(5.1)
the positions of the borderlines in the diagram (no SRO effects) correspond to
\[ \delta \mu^0_{SRO} = \delta \mu^b_{SRO}, \]  
(5.2)
while segregation suppression occurs when \( \delta \mu^0_{SRO} > \delta \mu^b_{SRO} \), and enhancement if \( \delta \mu^0_{SRO} < \delta \mu^b_{SRO} \). The FCEM correction (Eq. (3.24)) to the “p-layer chemical potential” Eq. (3.36) reads
\[ \delta \mu^p_{SRO} = -kT \sum_q z_{pq} c_q (1 - c_q) (1 - 2c_p) \left( \exp\left(-\frac{2V_{mn}}{kT}\right) + \frac{2V_{mn}}{kT} - 1\right), \]  
(5.3)
where the coordination number of a p-plane atom with respect to neighboring q-plane atoms is denoted by \( z_{pq} \) (the bulk coordination number is \( z = \sum_q z_{pq} \)). In case of equivalent surface and bulk nearest-neighbors interactions,
\[ \delta \mu^0_{SRO} = -kT [z_{00} c_0 (1 - c_0) + z_{01} c_1 (1 - c_1) (1 - 2c_0)] \left( \exp\left(-\frac{2V}{kT}\right) + \frac{2V}{kT} - 1\right), \]  
\[ \delta \mu^b_{SRO} = -kT z c (1 - c) (1 - 2c) \left[ \exp\left(-\frac{2V}{kT}\right) + \frac{2V}{kT} - 1\right], \]  
(5.4)
Therefore, according to Eq. (5.2) the borderlines in the SRO effect diagram correspond to
\[ [z_{00} c_0 (1 - c_0) + z_{01} c_1 (1 - c_1)] (1 - 2c_0) = z c (1 - c) (1 - 2c). \]  
(5.5)
Evaluation of the diagram is straightforward for the case of monolayer segregation, \( c_1 = c \), and for \( c_1 = c_0 \) in Eq. (5.5) (Fig. 24).

5.2. Surface segregation in Ni–Al solid-solution: the significant role of SRO

Probably the first clear experimental evidence for dominant effects of short-range order on surface segregation in a solid-solution concerns the peculiar segregation of aluminum in Ni–9%Al reported recently [19,158]. The segregation is significantly weaker than anticipated according to the BW-type pair-bond model, including elastic strain-energy contributions [48], and its equilibrium levels increase with temperature between \( \sim 500^\circ C \) and \( 750^\circ C \) (Fig. 25). Comparison of the data to calculations based on a segregation–kinetics model [159] with experimental diffusion coefficients of Al in Ni [160], showed that adequate equilibration was achieved even at the lowest annealing temperature. The distinct segregation trends, occurring at approximately the same temperature range for which significant short-range order was found to exist in Ni–Al solid-solutions by means of X-ray scattering, tensile strength and magnetoresistance measurements [161,162], has stimulated the attempt to compare the experimental data with theoretical predictions of SRO effects on surface segregation. Thus, the observed segregation behavior of aluminum could be fully accounted for in terms of the common Ising model extended to include SRO by means of the free-energy inverse-temperature expansion method (Section 3.4.2.1) [157,158]. In particular, Al layer concentrations (\( c_p \)) at the Ni–9%Al (110) surface,
Fig. 24. Calculated diagram of SRO enhancement (E)/suppression (S) effects on surface segregation in solid-solutions (relative to BW predictions) for f.c.c.(100) \((z_{00} = z_{01} = 4, z = 12, V_0 = V)\). Solid and dashed border lines correspond to the monolayer segregation approximation \((c_1 = c_0)\) and the assumption \(c_1 = c_{00}\), respectively. (i), (ii) and (iii) are the three bulk concentration ranges discussed in the text.

Fig. 25. Segregation kinetics of aluminum at the Ni–9%Al(110) surface as reflected in measured AES relative intensities. \((I_{Al}/I_{Ni} = 0.165\) for the alloy bulk composition.\) [19].
and at the less open (100) surface, were calculated in the \( \delta F_{2}^{\text{SRO}} \) approximation by means of the equilibrium segregation equations for solid-solution in the multilayer approximation derived in Section 3.5. Values for \( \Delta h_{0}, \Delta H_{0}^{\text{se}} \) and \( V \) were obtained from the pure Al and Ni surface tensions, atomic sizes, and their heat of mixing [163,164], respectively, and it was assumed that \( \Delta h_{p} = \Delta H_{p}^{\text{se}} = 0 \) for \( p \geq 1 \). As shown by electronic structure calculations [35], in Ni–Al solid-solutions the interactions are nearly the same at the surface and in the bulk. Since in the experiment the quite surface–sensitive Ni(MVV) and Al(LVV) low-energy Auger transitions have been chosen for quantitation, it is sufficient to include calculated signals from the three upper atomic layers, which contribute to about 95% of the total intensities. Thus, based on the \( c_{p} \) values derived, the intensity ratio for the alloy was calculated in the SRO approximation (and in the BW approximation), and is compared with the experimental data in Fig. 26. Clearly, SRO diminishes aluminum segregation levels, and the calculated ratios are significantly closer to the experimental results, including the peaked temperature dependence, resulting from the weakening of the suppression effect with increasing temperature. Since elastic strain energy

![Graph showing comparison of experimental and theoretical Auger intensity ratios of Ni–9%Al as function of equilibration temperature](image)

*Fig. 26. Comparison of experimental (●) and theoretical Auger intensity ratios of Ni–9%Al as function of equilibration temperature: (1) Bragg–Williams type approximation; (2) correlation (SRO) approximation, both with estimated \( \Delta h_{0} + \Delta H_{0}^{\text{se}} = -0.77 \text{ eV} \) [163]; (3) correlation approximation with fitted \( \Delta h_{0} + \Delta H_{0}^{\text{se}} = -0.68 \) and \(-0.79 \text{ eV} \) for (100) and (110), respectively (in all the calculations \( V = 0.15 \text{ eV} \)) [19].*
can be only roughly estimated, the surface field $H_0$ was determined by fitting to the experimental data, and as expected, the adjusted $\Delta h_0 + \Delta H_0^{\text{se}}$ absolute value for the more open (110)-surface, $0.79$ eV, is larger than the value ($0.68$ eV) obtained for the (100)-surface. Compositional variations with temperature in individual atomic layers, presented in Fig. 27, exhibit again the peaked temperature dependence characteristic of strong ordering/segregation competition. The oscillatory concentration profile obtained at all temperatures is related to the tendency of increasing the number of Ni–Al pairs in this ordering alloy. Compared to results of the BW-type calculations, the inclusion of SRO leads to significantly damped profiles that agree with conclusions in Section 3.5 and Fig. 5.

Numerical calculations for f.c.c.(100) based on the derived equations reveal quite subtle conditions for peaked temperature dependence of equilibrium surface segregation in solid-solutions. Thus, it is expected to occur in case the segregation is relatively weak, and it depends critically on the magnitude of the basic segregation driven-force ($\Delta h_0 + \Delta H_0^{\text{se}}$) relative to the solvent–solute interaction strength ($V$). Only when the ratio $R = |(\Delta h_0 + \Delta H_0^{\text{se}})/V|$ is not too large ($<\sim 10$ for this structure), significant SRO effects are expected, depending on the bulk concentration, the crystal structure as well as on the surface orientation. Another crucial factor is related to the interaction strength itself, since for alloys with relatively small $V$ the range of order-induced segregation suppression is expected to be well below temperatures required for achievement of surface segregation equilibration in reasonable annealing times (at higher temperatures, SRO effects become negligible). Both conditions for significant SRO segregation effects hold for Ni–Al solid-solutions. It should be noted, that, with exception of the size-mismatch contribution, $\Delta H_0^{\text{se}}$, the parameter $R$ for SRO effects is similar to the parameter $\Delta$ defined by

![Graph showing variations of Al relative enrichment (or depletion) at individual (100) atomic planes, as a function of temperature for Ni–9%Al with SRO (the outermost layer is denoted by 0, consecutive underlayers are marked by $p = 1,2,3$). The plane concentrations were calculated in accordance with the adjusted $\Delta h_0 + \Delta H_0^{\text{se}} = -0.68$ eV value and $V = 0.15$ eV [19].]
Eq. (4.1) [12] for the assessment of LRO effects. Indeed, the absence of any appreciable elemental enrichment in NiAl(111) was attributed to the relatively small value of $\Delta$ for Ni–Al (Section 4.1). So, in both the ordered and disordered states of this alloy the strong ordering tendency impedes segregation. Unlike the case of Ni–Al, very small deviations from the BW-type calculations were reported for Ag–Au and Ag–Pd solid-solutions [13,151], and for Ni–W [158]. Since the interaction parameters in these alloys are nearly an order of magnitude smaller than in Ni–Al, significant SRO effects can be expected only at very low temperatures. In a certain number of other binary alloys solute–solvent interactions are quite strong (e.g., Cr–Ni, or V–Sn), so that short-range order is expected to play a significant role in their measurable surface segregation characteristics.

5.3. Verification of the FCEM formula by Monte-Carlo simulations

As noted in Section 3.4.2.1, application of the inverse-temperature (cumulant) expansion (e.g., in the $\delta F_{2}^{\text{SRO}}$ approximation) can face a problem regarding the convergence of the truncated series. The free energy concentration expansion method (FCEM, Eq. (3.24)) on the other hand, is convergent, but was derived for the dilute limit, so its accuracy in predicting SRO effects was checked by comparison with Monte-Carlo simulations [20,83]. Calculations performed for the (100) face of f.c.c. solid-solution showed that the FCEM agrees with Monte-Carlo results better than both approximations based on the BW theory and the truncated inverse temperature series. In particular, even in the case of a non-dilute solution ($c = 0.09$) reasonable agreement was obtained, including the increase of equilibrium segregation level with temperature (Fig. 28a). As expected, the agreement improves gradually with lowering of the alloy bulk concentration and it becomes perfect for a dilute alloy with $c = 0.01$, as is shown in Fig. 28b.

In order to elucidate SRO effects, occupation pair probabilities for nearest-neighbor solute–solvent atoms, $p_{ij}^{\text{AB}}$, have been calculated vs. temperature for this structure with $(\Delta h_0 + \Delta H_0^c)/V = 3.87$, and are shown in Fig. 29. The difference between the FCEM results and the MC simulations for the dilute ($c = 0.01$) as well as non-dilute ($c = 0.09$) alloys is much smaller than their deviations from the BW predictions, which diminish with temperature due to SRO weakening. For the surface case (Fig. 29, left) the strong negative deviations from the random alloy values are associated mainly with the BW higher solute concentrations, while for the bulk (Fig. 29, right) the positive deviations represent “pure” correlation effects.

The accuracy of the proposed concentration expansion method was checked also by calculation of bulk properties, for which it again appears effective even beyond the dilute limit [20]. In particular, according to FCEM and MC calculated f.c.c. phase diagram the correct maximum $(kT_c/V = 0.9)$ of the $L1_2$–Al order–disorder transition temperature near the stoichiometric composition $c = 0.25$ is predicted [83]. Furthermore, in the FCEM (and MC) the concentrations of interest with respect to the above segregation calculations, $c = 0.01$–0.09, are in the region of a disordered solid-solution. In particular, the corresponding normalized transition temperatures vary between $\sim 0.0$ and 0.2, while the BW calculations give for the same concentration range $kT_c/V$ between $\sim 0.1$ and 0.8.

It should be noted that the FCEM analytical correlation approximation developed for the free-energy of dilute alloys has some practical advantages compared to the numeric MC computer simulations approach or the CVM approximation, both demanding much greater computational efforts. FCEM appears to give reasonable results even for non-dilute alloys, and it can be conveniently applied in systematic studies of SRO effects on surface segregation.
Fig. 28. Calculated results for the surface concentration of f.c.c.(100) solid-solution: $c = 0.09$ (a), $c = 0.01$ (b). Circles — MC simulations, solid lines — the FCEM approximation, dotted lines — the BW approximation. $(\Delta h_0 + \Delta H_0^c)/V$ are marked near the plots [20,83].

6. Order–disorder transitions

Starting with the low-temperature energetically favorable termination of ordered alloys, the structure and composition of the surface evolve with temperature, as reviewed in previous sections. In addition, near the bulk order–disorder temperature, the surface often exhibits a distinct behavior (a survey of surface transitions, illustrated by model calculations employing computer simulation techniques, can be found in [33]). In particular, in surface induced disorder (SID), the ordering in the top layer occurs at a lower temperature than in the bulk, or at the same temperature but the LRO near the surface is
Fig. 29. Calculated nearest-neighbor solute–solvent pair probabilities, \( p_{ij}^{AB} \), at the (100) surface (left) and the bulk (right) of f.c.c. solid-solution: (----) BW, (●) MC, (—) FCEM. In all calculations \( (\Delta h_0 + \Delta H_0^{\text{es}})/V = 3.87 \) [20,83].
diminished compared to the bulk. Due to the reduced symmetry, the surface can disorder continuously, while the bulk undergoes a first-order transition. In this case a disordered surface film ("wetting layer") emerges and grows in thickness as the transition temperature is approached from below.

On the other hand, in surface induced order (SIO), the temperature of the surface order–disorder transition is higher than the bulk value, or re-entrant surface order–disorder transition occurs, i.e., an ordered surface state separates from the region of ordered bulk in the concentration–temperature phase diagram. The phenomenon of oscillatory in-depth segregation profiles above the bulk transition temperature of ordering alloys can be also included in the category of SIO.

The occurrence of SID or SIO was analyzed theoretically using the Ising model [13–16]. Energetic parameters determining the segregation level and the position of the surface transition, \( T_s \), compared to the bulk, \( T_b \), are the surface field (\( H_0 \) in Ising model Hamiltonian (3.6)) and the relative strength of surface to bulk interactions, \( V_s/V \). The tetrahedron approximation of the cluster-variation method predicted disordering of the surface at temperatures above, below or at the bulk transition temperature [13]. In particular, surface/bulk phase diagrams (Fig. 30) were calculated for the stoichiometric \( A_3B \) system assuming \( V_s = V \) [14–16]. While the bulk transition is strongly first order, for \( T_s \leq T_b \) the LRO parameter at the (001) surface continuously decreases when the transition temperature (second-order) is reached from below, and thus a layer of a disordered phase at the surface is formed (SID with "wetting"). On the other hand, for surface concentrations around 0.5, \( T_s \) is higher than \( T_b \) (SIO) [14–16]. Monte-Carlo studies of surface induced ordering and disordering in \( AB \) alloys on a f.c.c. lattice revealed that occurrence of SIO or SID depends on the surface orientation, as shown in Fig. 31 [165]. In the following two sections, examples and origins of the phenomena are discussed in detail.

6.1. Surface induced disorder (SID)

Preferential disordering of the surface is expected because of the missing neighboring atoms, and it can penetrate into a depth controlled by a "correlation length". Studies of surface wetting and critical phenomena accompanying first-order bulk phase transitions, based on the Landau theory [166–168], predicted that the order parallel to the surface follows a power-low dependence, \( \psi_1 \sim t^\beta \), and the average wetting layer thickness can diverge logarithmically as \( \ln(1/t) \) with the reduced temperature \( t = (T_c-T)/T_c \) (Fig. 32). It should be noted that the mean-field theory predicts a critical exponent \( \beta = 1/2 \), which can change due to critical fluctuations, and according to the "universality hypothesis" is determined mainly by the symmetry and the dimensionality of the system [169]. The surface critical behavior depends on the surface orientation that preserves or breaks the two sublattice symmetry [170]. The wetting layer was studied by various computer simulations and related model calculations [171–173]. In order to elucidate the interplay of spatial order and segregation, the above studies of Lipowsky [166–168] were generalized [174,175], and it was argued that the disordering near-surface region does not diverge logarithmically as the transition temperature is reached from below, but the phase transformation evolves by a mechanism similar to phase separation in clustering alloys where two phases of different compositions coexist.

It should be noted that a logarithmical divergence of the antiphase boundaries in the bulk of a Cu–17%Pd alloy was observed (by TEM) when the first order L1_2–Al bulk transition temperature was approached from below [55,176]. However, for a second-order transition at the Fe–27%Al alloy boundaries, a different behavior consistent with the theoretically expected power law [177] was observed [178]. In the multilayer BW approximation applied to the Cu–Pd system, a wetting behavior
was revealed for the (111) surface second-order $L_{12} – A_1$ transition, while the $L_{12} – L_{10}$ surface transition remains first-order [179]. In case of the $L_{10} – A_1$ transition (first-order in the bulk), Monte-Carlo simulations show that for the (111) surface the order vanishes continuously (second-order) at the transition temperature of the bulk, and the transition is accompanied by critical wetting [180].

SID was studied extensively for the ordering alloy Cu$_3$Au as a model system, because it undergoes a first-order bulk $L_{12} – A_1$ transition at a temperature (663 K), well below its melting point. Distinct behavior was observed at different low-index surfaces of this alloy. A continuous surface transition starting 60 K below the critical temperature was found for Cu$_3$Au(100) using low-energy electron diffraction (LEED), and confirmed by Monte-Carlo calculations [181,182]. A number of experimental studies [105,183–187], as well as density functional calculations [188], are consistent with the major
Fig. 31. The temperature dependence of the surface-layer order-parameter (broken lines) and the bulk order-parameter (solid lines) calculated for $L \times L$ rectangular surfaces: (a) (100), and (b) (111) [165]. (The deviation between $L = 80$ and $L = 128$ reflects some finite size effects on the surface transition temperature, $T_{cs}$).

Fig. 32. Schematic normalized order-parameter profiles, $\eta(z)/\eta_b$, associated with surface-induced disorder. $\eta(z)$ and $\eta_b$ are, respectively, the order parameters at a depth $z$ and in the bulk, and $\xi_b$ is the correlation length. (a) Weak surface disordering (far from $T_c$); (b) advanced surface disordering (closer to $T_c$) with a delocalized wetting layer interface at a mean position $z = L$ from the surface [189].
findings. Moreover, in accordance with the theoretical predictions [166–168], a logarithmic growth of a disordered surface layer was observed [189,190] and wetting was indicated also by atomistic simulations [156]. According to LEED and LEIS data, the Cu$_3$Au(110) surface, on the other hand, undergoes a broadened discontinuous $2 \times 1 \rightarrow 1 \times 1$ transition at least 6 K below the bulk transition [191]. For the Cu$_3$Au(111) surface, glancing-angle X-ray-scattering experiments were interpreted as indicative of slight enhancement of the surface transition temperature (SIO) [120], and small (~2.5 nm) disordered clusters embedded in the ordered matrix at the surface region [121]. These domain-type fluctuations show that order is not uniform in-plane and varies smoothly with depth. More recent RHEED study of the (111) orientation found a surface order that varies continuously with a critical exponent in reduced temperature that agrees well with the mean-field prediction $\beta = \frac{1}{2}$ [122,123]. This indication that critical fluctuations are not so important is consistent with the fact that antiphase domain boundaries intersect the (111) surface. In contrast, the (100) surface, where the critical fluctuations can propagate without obstacles, displays $\beta \neq \frac{1}{2}$ behavior [184,186].

Peculiar surface-related features were found in Fe$_{71}$Al$_{29}$(110) [146,147], where the top three layers are strongly affected by surface segregation phenomena, with nearly pure Al segregated top layer (without LRO), and second and third layers exhibiting SIO (described in Section 6.2). Nevertheless, X-ray scattering data indicate preferential disordering in deeper layers, down to about 100 Å, and the surface critical exponents are in agreement with theoretical predictions for a non-segregated surface. Hence, it was concluded that due to the diverging correlation length, the surface critical behavior is rather insensitive to its microscopic features [147], in agreement with the universality hypothesis.

6.2. Surface induced order (SIO)

Since the ordering tendency at the surface plane is expected to decrease because of missing neighbors, other factors are required to offset this reduction in order to promote SIO. One possibility is the enhancement of the interactions at the surface plane. As calculations in the nearest-neighbor simple cubic Ising model show, the surface orders at a higher temperature than the bulk (SIO) only if the enhancement of the effective interactions in the surface plane exceeds the value $V_0 \approx 1.52V$ [192,193].

Another possible source of SIO (without alteration of surface interactions) is segregation-induced change of the state on the surface phase diagram (as in Fig. 30). Fe$_{71}$Al$_{29}$(110), mentioned in the previous section, shows such a phenomenon [146,147]. The Fe–Al system exhibits in the bulk phase diagram the DO$_3$(Fe$_3$Al)–B2(FeAl) transition in the Al concentration range $c_{Al} = 0.25–0.31$ (Fig. 33), and $T_c$ increases by 10 K for 1% decrease of the Al concentration. Due to extensive segregation, the top layer becomes totally saturated with Al and does not exhibit the ordered structure. However, since the segregating atoms come mainly from the second and third layers, their Al content decreases, and consequently the DO$_3$ phase survives up to temperatures of 16 K above the bulk $T_c$.

Segregation originated SIO can appear also in alloys with bulk concentration lower (or slightly higher) than the solubility limit. Application of the multilayer BW approximation with adapted TBIM energetic parameters to surface segregation in f.c.c.(111) revealed SIO over a disordered bulk in the case of low Sn concentration in Pt–Sn [194]. Moreover, the predicted $\sqrt{3} \times \sqrt{3}R30^\circ$ surface order (such as in Fig. 15a) differs from that of the (111) planes in the bulk L1$_2$ phase, (it was observed experimentally for sputtered–annealed Pt$_3$Sn(111) [108], Section 4.1). Enrichment of Pd at the surface of polycrystalline Fe$_{99}$Pd$_1$ was attributed to segregation from a two-phase bulk [195] with small fraction of ordered FePd acting as nuclei. The flux of segregating Pd to the surface causes gradual
growth of this phase until it covers the entire surface, yielding a nearly 50 at.% Pd composition. The observed increased segregation with temperature is characterized by positive entropy and energy (endothermic segregation), as suggested by Fig. 34. Another recent example of SIO over disordered bulk was reported for Li in Al–12.7 at.%Li(110) [196] exhibiting segregation-induced surface reconstructions (Fig. 35). The segregation seems to be endothermic, since the amount of surface Li increases with increasing annealing temperature (and time), but it is not clear whether the experiments involved adequate equilibration. Segregation originated SIO in underlayers is possible too as observed for the (110) surface of a Cu$_{85}$Pd$_{15}$ [7]. Furthermore, Cu segregation at the surface and a second layer exhibiting some degree of LRO above a disordered bulk were calculated recently by EAM–MC simulations for Cu$_{75}$Pd$_{25}$(110) [197].

For large surface fields and low bulk concentrations the appearance of SIO was predicted for the b.c.c.(110) surface in the BW approximation, revealing a re-entrant surface order–disorder transition above the transition temperature of the bulk crystal (Fig. 36) [198]. In particular, a region of ordered surface phase, c$(2 \times 2)$, that separates from the region of ordered bulk (for $T<T_b$), appears on the c–$T$
Fig. 34. Plot of \( \ln \left( \frac{c_0(1-c)}{c(1-c_0)} \right) \) vs. \( 1/T \) for Pd segregation at the surface of Fe_{99}Pd$_1$ solid-solution with less than 2% FePd nuclei. Fitted parameters: segregation energy \( \Delta U_0 = +14 \text{ kJ/mol} \), excess entropy \( \Delta S^\text{ex}_0 = +55 \text{ kJ/mol K} \) [195].

Fig. 35. \( T-t \) dependencies of Al–12.7at.%Li(110) surface reconstructions. Inset: schematic phase diagram according to the Li surface coverage [196].
phase diagram. The origin of this phenomenon can be understood by considering the variation with temperature of the surface segregation reaching sufficiently high levels (see also the surface/bulk phase diagrams in Fig. 30). A re-entrant surface transition was found by using the CVM tetrahedron approximation for various surface fields and surface to bulk relative interactions in f.c.c. (100) [17].

A possible SIO promoting factor is related to competing interactions in the bulk. In particular, the bulk transition temperature in f.c.c. AB binary alloys of the $L_{10}$ structure can be fairly low due to “frustrated” nearest-neighbor interactions in each triangle in the close-packed planes (Fig. 37). For a certain surface orientation, however, the interactions might not be frustrated, and a surface transition temperature higher than the bulk value can be expected [180]. Such a behavior was found using Monte-Carlo simulations for the $L_{10}$–A1 transition at different surfaces orientations [165, 199]: SIO at (100) with unfrustrated interactions (possibly related to segregation), in contrast to SID at the (111) surface with frustrated interactions (see Fig. 31).

A different kind of SIO can be introduced via the behavior of PdAg(100) revealed by STM [200]. Thus, the strongly enhanced Ag segregation from the solid-solution, resulting in Ag-terminated surface, was attributed also to the tendency to form the f.c.c. ordered structures $L_{10}$ or $L_{12}$, having (100) planes with alternating elemental concentrations (100%/0% and 100%/50%, respectively). Hence, the issue of SIO is somewhat related to the known phenomenon of oscillatory in-depth concentration profiles occurring in solid-solutions with ordering tendency ($V > 0$), where bonds between unlike atoms are an energetically favorable (Section 3.5). The segregation oscillations were predicted already in the BW (or “regular solution”) approximation [8, 9], and computed by MC simulations with bond-breaking energetics (for example [94, 201]). Such near-surface oscillations in composition were predicted for Pt–Ni alloys even well above the ordering region [202], in agreement with experiment [203], and for solid-solution CuAu(100) on the basis of MC calculations with an empirical interatomic potential (Fig. 38a) [26]. As can be seen, at lower temperatures the composition oscillations extend deeper into

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**Fig. 36.** Temperatures of the re-entrant surface order–disorder transition on b.c.c.(110) of $A_xB_{1-x}$ alloy as a function of $x$ for the case $V = 0.5$. “Surface field” related values, $W = V^{AA} - V^{BB}$, are marked near the plots. The broken line shows the bulk transition [198].
Fig. 37. Section of the ordered lattice of equiatomic AB alloy with the $L_{10}$ structure. Next-nearest-neighbor interactions are shown as solid lines, frustrated nearest-neighbor interactions are shown as dashed lines, while unfrustrated nearest-neighbor interactions are not marked. A and B atoms are denoted as open and full circles, and the orientation of the coordinate axes is indicated together with the {100} surface [180].

Fig. 38. Oscillatory (decaying) segregation profiles near and above the order–disorder transition temperature: (a) (left) calculated profile for CuAu(100) surface in a 15-layer slab. $T_c$ estimated from bulk simulations is around 800 K (the experimental value is $\sim$680 K) [26]; (b) (right) Cu$_3$Au(100) profile, as resolved by X-ray scattering experiments [206]. The vertical axis denotes the layer dependent excess (or deficiency) in Au concentration. Both profiles decay to the average bulk value and the exponential decay length decreases distinctly upon heating.
the slab. Recently, a deep layer oscillatory segregation (and relaxation) in Mo$_x$Re$_{1-x}$(001) with first-layer segregated Mo was detected using quantitative LEED [204], and predicted theoretically [205]. The appearance of the “oscillatory SIO” above $T_c$ does not prevent SID below $T_c$, as observed for Cu$_3$Au(100). In particular, since the surface favors a laterally homogeneous Au enrichment, the in-plane order parameter components $\psi_1$ and $\psi_2$ (Section 2.2) vanish in the “wetting layer” (Section 6.1) appearing when the temperature is close to $T_c$ (SID). X-ray scattering studies [42,206] show, however, that the perpendicular $\psi_3$-component does not disappear at the surface at $T > T_c$. It rather remains non-zero within the whole surface layer whose thickness is controlled by the bulk correlation length of the disordered Cu$_3$Au phase (Fig. 38b). The decay length diverge at $T_c$ since the direction perpendicular to the surface orientation corresponds to compositional oscillations in the ordered $L1_2$ phase bulk appearing at and below $T_c$. A final note about kinetics: according to a time-resolved X-ray scattering study, the symmetry break induced by the presence of a free surface has large influence on the ordering kinetics [207]. Thus, the oscillatory SIO layered structure in Cu$_3$Au(100) is formed at the surface and propagates immediately into the bulk, while lateral order is built up in a slow nucleation and growth process, initiated in the bulk and proceeding to the external surface.

6.3. Phase transitions and segregation in thin films and nano-particles

During recent years, thin films and nano-particles have attracted growing attention due to possibilities of tailoring specific size-dependent physical properties with potential applications. The interplay of surface segregation and LRO can become even more complex in systems with restricted dimensions, when this additional intrinsic factor plays a role. Already early Monte-Carlo results showed that the degree of surface segregation in thin films and small particles tend to be smaller than in semi-infinite slabs [94]. Recently, calculations of the surface composition in the intermetallic compound MgNi$_2$, introduced in Section 4.2, revealed significant effects of the film thickness on the segregation level [150], as is shown in Fig. 39. Thus, the segregation levels increase with thickness and the effect of temperature becomes stronger, without changing the general trends. All these sample dimension (size) effects are clearly related to variations in the overall reservoir of atoms available for segregation, which becomes meager for thinner films or smaller particles. Other calculations showed that competition between surface segregation and bulk ordering in (100) thin films of $AB$ b.c.c ordering alloys, can cause formation of metastable states with antiphase boundaries [208,209]. Although the intrinsic surface segregation tendency in nano-particles is smaller than in semi-infinite alloys, it can still be dominant in the overall segregation/order competition, since the tendency for ordering is reduced too. A study of ordering and segregation interplay in bimetallic nano-clusters within the regular solution model revealed that the atomic spatial distribution is strongly affected not only by the pertinent energetic parameter $\Delta$, as defined in Section 4.1, but also by the “dispersion”, defined as the ratio of the number of surface atoms, $N_S$, to the total number of atoms, $N$, in the cluster ($D = N_S/N$ is larger for smaller clusters). In case of large $D$, the existence of segregated and ordered phases that are uniquely characteristic of small clusters is predicted (although in nano-systems, “phases” are not sharply defined) [210]. For example, in A–B icosahedron composed of 55 atoms, all the A atoms segregate to its surface in case of very small $\Delta^{-1}$, as is shown in Fig. 40, whereas a dominant ordering behavior was predicted for particles with relatively large $\Delta^{-1}$. It was found that due to the small size, the segregation tendency in the Cu–Pd and Ni–Pt nano-clusters, can overwhelm the tendency to order (in macroscopic systems both form ordering alloys [211]).
Unlike the case of a bulk alloy with a surface, a thin film is expected to have only one transition temperature [212], so the issues of SID and SIO in thin films can be considered in two ways: either to compare the transition temperature and average order in the film with the bulk values (for the infinite alloy), or to compare the degree of order at the film surface with the rest of the planes. Average order below the bulk value [208,209] can be considered as a sort of SID. On the other hand, the film surface can have a larger degree of order while the rest of the planes are practically disordered, resembling SIO [212].

Studies of phase transitions in b.c.c.(110) binary alloy thin films in the BW-type approximation [212] revealed factors that promote the increase of $T_c$ compared to the bulk value (similarly to the SIO factors in semi-infinite alloys, Section 6.2): (i) strong surface segregation of one of the components, and (ii) enhanced surface interactions that exceeds a critical value. Otherwise, the reduced order–disorder phase transition temperature $T_c(N_f)$ monotonously increases with number of layers $N_f$ up to the bulk value, $T_c(\infty)$ (Fig. 41 (bottom)). In case of low solute concentrations, $T_c(N_f)$ can exhibit a maximum for small film thickness that exceeds the bulk value (SIO, Fig. 41 (top)) [212]. This peculiar behavior was attributed to solvent surface segregation that increases the solute concentration in the subsurface planes.

Finally, phase transitions characteristic to thin films of “phase-separating” binary alloys ($V < 0$), treated within the BW approximation [213], are briefly described. At low temperatures, an inner

Fig. 39. The film thickness dependence of the calculated surface concentration vs. temperature for MgNi$_2$. Segregation levels increase with thickness due to the increased overall reservoir of atoms in the film [150].
Fig. 40. Phase diagram for icosahedral 55 atom bimetallic A–B cluster (composed of four "shells") in terms of the number of A atoms, \( N_A \), and of the relative ordering/segregation driving forces, \( \Delta^{-1} = (V_{AA} + V_{BB} - 2V_{AB})/(V_{AA} - V_{BB}) \). The phases are ordered (O) or segregated (S), and the sub-indices denote the consecutive shells where B atoms are substituted by segregating A atoms (3: refers to the outmost shell, 0: to the atom in the cluster center). The symbols (●), (▲) and (▼) correspond to the \( \Delta^{-1} \) parameters of Cu–Pd, Ni–Pt and Cu–Ni, respectively [210,211].

Fig. 41. Normalized order–disorder transition temperature, \( T_c(N_f)/T_c(\infty) \), calculated as function of film thickness, \( N_f \), for two concentrations, \( x = 0.1 \) and 0.4, in b.c.c.(110) \( A_xB_{1-x} \) alloy (unaltered surface interactions, \( V_s = V \)) [212].
interface between $A$-rich and $B$-rich phases was predicted, and its location depends on the overall concentration. For each concentration, and depending on the number of layers in the film, a second-order transition occurs for which, at a certain “symmetrization temperature”, the interphase interface disappears and the concentration profile becomes symmetric with respect to the center of the film (Fig. 42A). Furthermore, in case of symmetric concentration profiles, and depending on concentration, transitions from homogeneous to inhomogeneous profiles were predicted by TBIM–BW studies of Cu$_x$Fe$_{1-x}$(110) thin films [214] (Fig. 42B).
7. Summary

The concurrent tendencies of surface segregation and atomic ordering in metallic alloys can be manifested in a variety of phenomena, involving significant deviations from the segregation characteristics of random solid-solutions, and from the bulk-like near-surface atomic or compositional order. Thus, long-range order (LRO), and in some cases also short-range order (SRO), can impede segregation in alloys with elemental mixing tendency, or alternatively, strong segregation tendency can disrupt LRO. In a different situation, segregation from a disordered bulk can lead to enhanced order at the surface.

The analogy between LRO and elemental enrichment/depletion (both involving *entire* lattice layers parallel to the surface) is helpful in the unified description of these phenomena by means of adapted statistical-mechanical methods, which were developed originally for characterization of bulk order. The simplistic bond-breaking model for monolayer segregation used in early studies was improved by including multilayer in-depth compositional gradients as well as LRO by means of BW-type approximations. SRO effects in ordered alloys and in solid-solutions were accounted for by means of the cluster variation method (CVM), or by Monte-Carlo simulations, both having somewhat limited applicability in the surface segregation issue, mainly due to computational difficulties. The more recently adapted free-energy expansion method offers interesting perspective for a systematic study of SRO effects on surface segregation, using formulae derived in detail in this review. Experimental study of the segregation order interplay requires state of art techniques that provide layer-by-layer data about shallow compositional gradients up to the outmost surface layer, and pertinent information regarding near-surface order.

Segregation ordering interrelated phenomena can be divided among three main categories: the surface basic compositional termination in ordered alloys, its temperature dependence up to disordering (including surface-induced disorder and surface-induced order), and effects of SRO on surface segregation in solid-solutions.

7.1. The surface termination

Although theoretically this concept refers to very low temperatures (no entropy effects), practically, measurements at higher temperatures are needed for equilibration in reasonable acquisition times. In most cases the surface termination of alloys with LRO at low or intermediate temperatures is determined by a *competition* between ordering and segregation tendencies. The latter factor often minimizes the alloy surface tension, but in case of relatively strong tendency to order segregation does not occur (or elemental surface tension still controls which of possible ordered terminations is the most stable). Theoretical approaches to the problem define quantitative criteria by means of the relationship between energetic parameters, such as the segregation driving forces vs. the interatomic interaction strength, which governs the ordering tendency. As described in Section 4 (and using its terminology), one can distinguish between several principal types of surface termination in ordered alloys:

1. Pure element termination.
   1.1. BTO_{P} in structures with at least two possible surface terminations of the bulk order. In this case of surface layer corresponding to bulk truncated order, the segregation and ordering tendencies seem to be compatible (e.g., the experimentally determined f.c.c.-based L1_{2} alloys: Cu in Cu_{3}Pt(100), Pt in Pt_{3}Ti(100) and Au in Au_{3}Pd(100)).
1.2. NBTp: in case of very strong elemental segregation tendency (that sometimes cannot be explained by simple surface tension considerations), the ordering tendency is impeded. The pure element surface layer and the near-surface compositional oscillations do not correspond to bulk truncated order (e.g., the DO3 structure is disrupted by pure Al segregated surface layer in Fe71Al29(110)).

2. Stoichiometric termination corresponding to bulk truncated order, BTOs (no surface segregation). In most of the examples a single surface termination of the bulk order is possible (e.g., Cu3Au(111), Cu3Pt(111) and Ni3Al(111)). In this case, the ordering tendency impedes surface segregation.

3. Non-stoichiometric mixed surface layer termination.
   3.2. BTO M in structures with at least two possible surface terminations of the bulk order. The surface segregation tendency can promote a mixed layer termination enriched (beyond the bulk stoichiometry) by the constituent with the lower surface tension. The ordering tendency impedes further segregant enrichment beyond the bulk-truncated concentration (e.g., Au in Cu3Au(100), Sn in Pt3Sn(100) and Al in Ni3Al(100)).

3.3. NBT M: the termination does not correspond to bulk truncated order, which is disrupted by segregation. This case has some resemblance to case 1.2, but the segregation tendency is not strong enough to create a pure element termination. (e.g., Cu segregation in Cu3Pt(110) and Au in Cu3Au(110)).

7.2. The temperature dependence

Variations in the equilibrium surface composition of ordered alloys with temperature depend on interatomic energetic parameters, the surface orientation and its prior, low temperature termination. In case the segregation process is endothermic and the low-temperature termination corresponds, for example, to bulk truncated order with no surface segregation (BTOs), entropy-driven segregation that grows with temperature is expected. Since order is diminished with increasing temperature, the process can become exothermic and the surface concentration of the segregant eventually starts to decrease (the maximum should occur near or at the order–disorder phase transition temperature). Experimental observations of the theoretically anticipated peaked segregation vs. temperature curve are scarce (e.g., Au in Cu3Au(100) and Al in NiAl(100)).

The entropy increase at high temperatures can be accompanied by the phenomena of surface-induced disorder (SID, due to missing bonds) or surface-induced order (SIO, originated from enhanced surface or frustrated bulk interactions), both of which should be affected by surface segregation. In SID, the temperature of the surface order–disorder transition, or the degree of order at the surface, are lower than the bulk value, while in SIO they are higher. Both SIO and SID can be accompanied by a change in the type of the transition compared to the bulk behavior. Oscillatory segregation profiles often observed and predicted for ordering alloys above $T_c$, can be classified as a sort of SIO.

In samples with restricted dimensions the segregation-order interplay can be expected to be somewhat more complex because of the additional intrinsic factor (besides average concentration, energetic parameters, etc.). According to model calculations both the degree of surface segregation and atomic order in thin films and nano-particles tend to be smaller than in macroscopic alloy samples. Possible decrease of the average film order (or $T_c$) with diminishing thickness below the corresponding bulk values can be classified as a sort of SID. On the other hand, a thin film surface can exhibit large degree of order while the rest of planes are practically disordered (resembling SIO). For certain
energetic parameters in nano-particles the segregation tendency can overwhelm the tendency to order, unlike the situation in the corresponding macroscopic alloys.

7.3. Short-range order effects in solid-solutions

Some order segregation interplay can persist even above the order–disorder transition temperature as SRO effects can impede (or slightly promote) surface segregation. The compositional fluctuations associated with SRO always attract solute atoms, and thus ordered clusters are able to grow in the bulk or at the surface. Similarly to the LRO case, a subtle balance of segregation driving-forces and interaction strength controls the segregation level and its variation with temperature. In case of relatively strong interactions and weak segregation tendency in a non-dilute solid-solution, the segregation of a solute can be suppressed because of its stronger attraction to bulk fluctuations compared to surface fluctuations. Since this suppressing effect decreases along with SRO at higher temperatures, an increase in equilibrium segregation level becomes possible, as observed for Ni–Al solid-solution. This endothermic process results in the SRO analog to the LRO-induced peaked segregation temperature dependence. Based on numerical evaluations, short-range order is expected to play a significant role in surface segregation characteristics of a certain number of binary alloys with quite strong solute–solvent interactions, but in many other systems the role of SRO should be minor.

To conclude, the report tried to highlight the considerable progress made during recent years in elucidating the role of atomic order in surface segregation phenomena in metallic alloys (without relating to other materials, such as semiconductors [215]). Still, various issues regarding the low temperature stable termination of ordered alloys, the temperature dependencies of segregation and near-surface atomic order, as well as surface phase transitions, including thin films and nano-particles, need further theoretical and experimental efforts. Deeper insight into several surface-composition/order related phenomena (e.g., surface magnetism, adsorption, etc.) could be gained by extending the present unified segregation/ordering description to include pertinent energetic and entropic contributions.

Note added in proof

One more case of peaked segregation curve (see Sections 3.6, 4.1 and 5.2) related to the interplay of surface segregation and ordering, was reported for an Al-3%Ag alloy equilibrated between 550 and 770 K [M. Erbudak, M. Hochstrasser and E. Wetli, J. Electron Spectr. Related Phenom. 76 (1995) 529]. It was attributed to segregation enhancement of small Ag$_2$Al-like clusters with increasing temperature, their dissolution (first-order phase transition), and Ag desegregation at the highest temperatures.

References

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