Chapter 4
Models of Equilibrium Grain Boundary Segregation

4.1 Thermodynamics of Grain Boundary Segregation

Interfaces, in general, represent structural defects of a crystal characterised by existence of unsaturated bonds. Therefore, the Gibbs energy of an interface will be higher than the Gibbs energy of the single crystal containing the same ensemble of atoms. The value of the Gibbs energy of an interface depends on various variables, particularly on its energy (i.e. type, orientation and atomic structure), composition, temperature and pressure. To minimise the total Gibbs energy of the system (i.e. Gibbs energy of the interface plus Gibbs energy of the volume), the interface interacts with other lattice defects such as dislocations, vacancies and foreign atoms. As mentioned previously, the latter interaction results in accumulation of the solute atoms in the interface region and is called *interfacial segregation* (e.g. [12, 19, 20]). As individual types of the interfaces possess the same nature (i.e. planar defects), the interaction of individual types with foreign atoms is expected to be qualitatively similar.

As was mentioned in Chap. 2, two basic forms of grain boundary segregation can be distinguished: *equilibrium* and *non-equilibrium* segregation. Equilibrium segregation occurs as a result of inhomogeneities in the solid giving rise to sites for which solute atoms have a lower Gibbs energy. These sites occur at interfaces such as free surface, grain boundaries and phase interfaces as well as at defect sites, dislocations and stacking faults. All of these regions then may exhibit concentrations of solute atoms that differ from each other and from that of the bulk materials. At any temperature, there is a unique value of the solute concentration for each of these sites that is asymptotically approached as time goes to infinity and at a rate governed by diffusion. On the other hand, non-equilibrium segregation depends on rate processes and kinetic events and, in general, disappears as time approaches infinity if diffusion processes are allowed to reach full equilibrium. There are number of discrete routes for producing this form of segregation, which include moderate rate quenching of samples from a high temperature, the growth of precipitates, the effect of stress at temperature, etc. In this chapter, we will deal with equilibrium segregation.

Phenomenological description of equilibrium segregation is qualitatively the same for all types of interfaces. The differences arise concerning the values of particular thermodynamic parameters resulting from different structural/bonding conditions at individual cases [299–301]. In the following, we show two main approaches to the thermodynamic description of the grain boundary segregation, the *Gibbs adsorption isotherm* and the *Langmuir–McLean types of segregation isotherm* (e.g. [13, 19, 20]).

4.2 Gibbs Adsorption Isotherm

Let us consider a macroscopic system large enough to keep constant pressure and plane interfaces [302]. Integration of (2.20) accounting Euler theorem results in

$$U = TS - PV + \sum_{i=1}^{N} \mu_i n_i + \sigma A. \tag{4.1}$$

Its differentiation and comparison with (2.20) provides us with the relationship

$$A\mathrm{d}\sigma = -S\mathrm{d}T + V\mathrm{d}P - \sum_{i=1}^{N} n_i \mathrm{d}\mu_i. \tag{4.2}$$

Let us note that (4.1) and (4.2) are related to the whole system. Since the Gibbs–Duhem equation

$$-S\,\mathrm{d}T + V\,\mathrm{d}P - \sum_{i=1}^{N} n_i \mathrm{d}\mu_i = 0 \tag{4.3}$$

is valid for each homogeneous phase [104], it should also be valid for both grains A and B,

$$-S^A \mathrm{d}T + V^A \mathrm{d}P - \sum_{i=1}^{N} n_i^A \mathrm{d}\mu_i = 0 \tag{4.4}$$

and

$$-S^B \mathrm{d}T + V^B \mathrm{d}P - \sum_{i=1}^{N} n_i^B \mathrm{d}\mu_i = 0. \tag{4.5}$$

Comparison of (4.4) and (4.5) with (4.2) gives

$$-s^\Phi \mathrm{d}T + v^\Phi \mathrm{d}P - \sum_{i=1}^{N} \Gamma_i^\Phi \mathrm{d}\mu_i + \mathrm{d}\sigma = 0 \tag{4.6}$$

where s^Φ, v^Φ and $\Gamma_i^\Phi = n_i^\Phi / A$ are the entropy, the volume and the amount of the component i at the grain boundary Φ, respectively, all normalised by the grain boundary area. The quantity Γ_i^Φ is, thus, the *surface density of the solute i at the* *interface* as introduced by Gibbs [101] or the *adsorption* as used by McLean [19]. Much later, a term *grain boundary excess* of component i was introduced. This terminology is very unlucky as discussed in more detail in Sect. 4.3. Therefore, we will use the term *adsorption* for Γ_i^Φ.

Let us define the interfacial quantities of the system as

$$U^\Phi = U - (U^A + U^B), \tag{4.7}$$

$$S^\Phi = S - (S^A + S^B), \tag{4.8}$$

$$n_i^\Phi = n_i - \left(n_i^A + n_i^B\right) \tag{4.9}$$

and

$$V^\Phi = V - (V^A + V^B) = 0. \tag{4.10}$$

The value of V^Φ is zero by definition ($V = V^A + V^B$). Combining (4.7)–(4.10) with (2.20) and subsequent expressions,

$$\mathrm{d}U^A = T\,\mathrm{d}S^A - P\,\mathrm{d}V^A + \sum_{i=1}^{N} \mu_i \mathrm{d}n_i^A \tag{4.11}$$

and

$$\mathrm{d}U^B = T\,\mathrm{d}S^B - P\,\mathrm{d}V^B + \sum_{i=1}^{N} \mu_i \mathrm{d}n_i^B \tag{4.12}$$

produces

$$\mathrm{d}U^\Phi = T\,\mathrm{d}S^\Phi + \sum_{i=1}^{N} \mu_i \mathrm{d}n_i^\Phi + \sigma\,\mathrm{d}A. \tag{4.13}$$

The analysis in [12, 103] shows that all relationships between thermodynamic quantities are applicable to the systems containing grain boundaries when the interfacial characteristics – the grain boundary energy σ – is taken into account and that these relationships are independent of the thickness of the grain boundary.

Combination of (4.6) with the Gibbs–Duhem condition $\Sigma_i n_i \mu_i = 0$ results for a binary system ($i = M, I$) in an interesting relationship for adsorption Γ_i^Φ

$$\frac{n_I}{n_M}\Gamma_M^\Phi - \Gamma_I^\Phi = \left(\frac{\partial \sigma}{\partial \mu_I}\right)_{T,P}. \tag{4.14}$$

Equation (4.14) can be simplified for case of $\Gamma_M^\Phi = 0$ as

$$\Gamma_{I,M}^\Phi = -\left(\frac{\partial \sigma}{\partial \mu_I}\right)_{T,P}, \tag{4.15}$$

where $\Gamma_{I,M}^{\Phi}$ indicates the above condition $\Gamma_M^{\Phi} = 0$ [303]. It follows from (4.6) that the element, which causes a decrease of the grain boundary energy with increasing chemical potential, accumulates (segregates) at the grain boundary [12].

Substituting the chemical potential μ_i by the activity a_i according to the expression [104]

$$\mu_i = \mu_i^0 + RT \ln a_i, \tag{4.16}$$

where μ_i^0 is the standard chemical potential of element i in the bulk and R is the universal gas constant, we obtain [138, 303]

$$\Gamma_{I,M}^{\Phi} = -\frac{1}{RT}\left(\frac{\partial \sigma}{\partial \ln a_I}\right)_{P,T}. \tag{4.17}$$

In the dilute approximation, which is that of general interest, for a bulk solute molar concentration $X_I \ll 1$, in which $a_I = \gamma_I X_I$ [304] with the activity coefficient $\gamma_i \approx 1$, this becomes

$$\Gamma_{I,M}^{\Phi} = -\frac{1}{RT}\left(\frac{\partial \sigma}{\partial \ln X_I}\right)_{P,T}. \tag{4.18}$$

Equation (4.18) provides us thus with a simple relation between adsorption $\Gamma_{I,M}^{\Phi}$ on the one hand and the change of the interfacial energy σ with the molar fraction X_I of the solute in bulk on the other hand. Equation (4.18) is the most useful form of the *Gibbs adsorption isotherm* for a dilute binary system. This basic form has been used experimentally to determine the interface density of the solute I from the changes of the grain boundary energy with changing the bulk composition for all interfaces in solids [13].

The Gibbs adsorption isotherm was successfully applied to quantify the first experiments on grain boundary segregation, for example on phosphorus in γ-iron [305] and tin [306, 307], silicon and sulphur in δ-iron [308]. However, the measurement of the surface energy as a function of both the bulk concentration and the temperature is rather difficult. Therefore, many attempts have been made to develop alternative phenomenological models of grain boundary segregation based on simple relationships between interfacial and bulk compositions.

$\Gamma_{I,M}^{\Phi}$ is also frequently used to represent grain boundary segregation measured by APFIM methods (e.g. [231,239,303,309]). In order to describe interfacial chemistry in binary as well as multi-component systems, it is useful to generalise the measured quantities. Therefore, the *grain boundary enrichment ratio*, β_I^{Φ}, is defined as the ratio between the grain boundary and the bulk solute concentrations, $X_I{}^{\Phi}$ and X_I, respectively $\left(X_I^{\Phi} \gg X_I\right)$ [13],

$$\beta_I^{\Phi} = \frac{X_I^{\Phi}}{X^0 X_I} = \frac{\Gamma_I^{\Phi}}{\Gamma^0 X_I}, \tag{4.19}$$

where Γ^0 is the maximum amount of solute constituting a close packed monatomic layer of unit area and X^0 is the maximum grain boundary atomic concentration of the solute.

4.3 Langmuir–McLean Types of Segregation Isotherm

This approach is based on equality of chemical potentials (Gibbs energy) of the components in equilibrium. There exist several ways to derive the segregation isotherms based on this approach; however, some of them are thermodynamically inconsistent although all of them provide very similar results. We will follow the way presented by duPlessis and van Wyk [302, 310, 311].

Let us consider a closed system containing the grain boundary inside the crystalline surrounding. The grain boundary is considered as a region of finite thickness, while the bulk of the crystal is of infinite size. Grain boundary segregation is then defined as a redistribution of solute atoms between the crystal and the interface: From this point of view, both parts of the system are considered as open enabling an exchange of the solutes. In equilibrium, the system as a whole must possess minimum energy. The variations of the total internal energy δU of the closed system is given by

$$\delta U = \sum_{\nu} \delta U^{\nu} = \sum_{\nu} (T^{\nu} \delta S^{\nu} - P^{\nu} \delta V^{\nu} + \delta G), \tag{4.20}$$

where T^{ν} is the temperature, S^{ν} is the entropy, P^{ν} is the pressure and V^{ν} is the volume of the structural component ν of the system (i.e. of the crystal volume and the grain boundary). G is the Gibbs energy of the system. If the temperature and pressure are the same in all these structural components and the equilibrium state is reached, (4.20) reduces to [104]

$$(\delta U)_{n_j} = (\delta G)_{n_j} = 0, \tag{4.21}$$

where n_j is the number of moles of the solute j. If the crystal is divided into $N + 1$ open subsystems (N in bulk, one for the grain boundary) and the redistribution of the solutes occurs, duPlessis and van Wyk showed in very detail that the Gibbs energy of the system is given by

$$G = G_{\mathrm{B}} + \sum_{i=1}^{M} n_i^{\Phi} \left(\mu_i^{\Phi} - \mu_i^{B} \right), \tag{4.22}$$

where n_i^{Φ} is the number of moles of solute i in the grain boundary, and μ_i^{Φ} and μ_i^{B} are the chemical potentials of the ith solute in the grain boundary and in the bulk. The number of the solutes is M. In (4.22), the Gibbs energy G_{B} (equal to the

Gibbs energy of the bulk before segregation) is independent of changes of n_i^Φ and the sum in (4.22) represents the product of the grain boundary energy σ and the grain boundary area A [302, 310, 311]

$$\sigma A = \sum_{i=1}^{M} n_i^\Phi \left(\mu_i^\Phi - \mu_i^B\right). \tag{4.23}$$

It follows from (4.22) and (4.23) that

$$G = G_\mathrm{B} + \sigma A. \tag{4.24}$$

Since G_B is constant in respect to n_i^Φ, the equilibrium condition $\partial G/\partial n_i^\Phi = 0$ can be written as

$$\frac{\partial\sigma}{\partial n_i^\Phi} = 0. \tag{4.25}$$

Equation (4.25) shows that *in equilibrium, the grain boundary energy possesses the minimum value* [302, 310, 311].

The equilibrium condition can be expressed as

$$\frac{\partial\sigma}{\partial n_1^\Phi} = \frac{\partial\sigma}{\partial n_2^\Phi} = \cdots = \frac{\partial\sigma}{\partial n_M^\Phi} = 0. \tag{4.26}$$

However, the conditions (4.26) are not independent because

$$n_1^\Phi + n_2^\Phi + \cdots + n_M^\Phi = n^\Phi, \tag{4.27}$$

that is the number of moles n^Φ in the finite grain boundary region is constant. Supposing M is referred to the matrix element and $n_M^\Phi = 1 - \sum_{i=1}^{M-1} n_i^\Phi$, the basic condition for chemical equilibrium between the grain boundary Φ and the volume B is [302, 310, 311]

$$\Delta G = \left(\mu_i^\Phi - \mu_i^B\right) - \left(\mu_M^\Phi - \mu_M^B\right) = 0 \tag{4.28}$$

for each component $i = 1, 2, \ldots, M-1$ despite of their number.

Combining (4.16) and (4.28), the general form of the segregation equation can be written as

$$\frac{a_I^\Phi}{a_M^\Phi} = \frac{a_I}{a_M}\exp\left(-\frac{\Delta G_I^0}{RT}\right). \tag{4.29}$$

In (4.29) the *standard* molar Gibbs energy of segregation,

$$\Delta G_I^0 = \left(\mu_M^0 + \mu_{I(M)}^{0,\Phi}\right) - \left(\mu_{I(M)}^0 + \mu_M^{0,\Phi}\right) \neq 0 \tag{4.30}$$

is defined as a combination of the standard chemical potentials of the elements I and M in pure state at the grain boundary and in the bulk, ${\mu_i}^{0,\Phi}$ and μ_i^0, respectively, at the temperature and pressure of the system and *in the structure of the matrix element* (as is indicated by index (M) in brackets). Since generally,

$$a_i = \gamma_i X_i, \tag{4.31}$$

where γ_i is the activity coefficient of an element i, [304], we can write (4.29) using $X_M = 1 - \sum_{J=1}^{M-1} X_J$ as

$$\frac{X_I^\Phi}{1 - \sum\limits_{J=1}^{M-1} X_I^\Phi} = \frac{X_I}{1 - \sum\limits_{J=1}^{M-1} X_I} \exp\left(-\frac{\Delta G_I^0 + \Delta G_I^{\mathrm{E}}}{RT}\right). \tag{4.32}$$

In (4.32),

$$\Delta G_I^{\mathrm{E}} = RT \ln\left(\frac{\gamma_I^\Phi \gamma_M}{\gamma_I \gamma_M^\Phi}\right) \tag{4.33}$$

ΔG_I^{E} is the *excess* molar Gibbs energy of segregation. Since (4.32) was derived without any assumption about the character of the system, t represents the *general form of the segregation isotherm.*

The thermodynamic representation of the grain boundary segregation is schematically depicted in Fig. 4.1. In Fig. 4.1, the concentration dependence of the Gibbs energy of the crystal volume (*bulk*) and of the grain boundary (Φ) is shown. Since the grain boundary represents the defect of crystal structure, it has to possess higher Gibbs energy comparing to the bulk in the whole concentration range of the binary system. Thus, the concentration dependence of the Gibbs energy of the grain boundary is "shifted" to higher values in comparison to a similar dependence of the Gibbs energy of the bulk. Because the grain boundary does not represent another phase, the equilibrium between the boundary and the bulk is not given by a common tangent as in phase equilibrium. To fulfil condition (4.28), the grain boundary concentration, X_I^Φ, is defined by the tangent to the Gibbs energy of the grain boundary, $G^\Phi(X)$, parallel to that for the bulk, G^{bulk}, at the concentration X_{bulk}. On the other hand, $\Delta G_I^0 = \left(\Delta\mu_{I(M)}^{0,\Phi} - \Delta\mu_{I(M)}^0\right) - \left(\Delta\mu_M^{0,\Phi} - \Delta\mu_M^0\right) \neq 0$ (cf. Fig. 4.1). It directly follows from (4.30) and Fig. 4.1 that ΔG_I^0 as the sum of the standard chemical potentials of pure substances is *independent of composition* of the system, and further, that $\mu_i^{0,\Phi}$ and μ_i^0 represent respective molar Gibbs energies, that is they are composed of the terms of both the standard enthalpy and the standard entropy of pure elements in the chosen standard states.

The above derivation differs from that presented sometimes in other papers (e.g. [20, 301, 310, 312–316]). There, the chemical potential for the interface is

$$\mu_i^{0\Phi} = \xi_i^{0\Phi} + RT \ln a_i^\Phi - \sigma A_i. \tag{4.34}$$

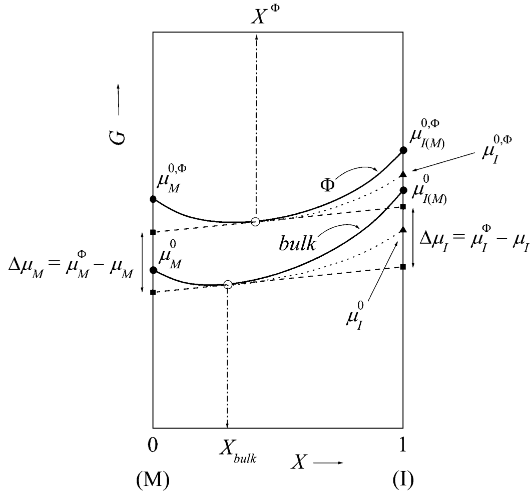

Fig. 4.1 Schematic depiction of the concentration dependence of the Gibbs energy of the volume (*bulk*) and the grain boundary (Φ) leading to representation of the Gibbs energy of segregation. ΔG_I^0 is defined by (4.30). $\mu_{I(M)}^{0,\Phi}$ and $\mu_{I(M)}^{0}$ correspond to the respective states of pure I in the structure of the interface and bulk of M and are higher than the respective values of $\mu_i^{0,\Phi}$ and μ_I^0, corresponding to the structures of pure I. The equilibrium concentration X_I^{Φ} is defined by the tangent to G^{Φ} parallel to that of G^{bulk} constructed in X_I. This conserves the condition $\Delta G = \Delta\mu_I - \Delta\mu_M = 0$ for each pair X_I and X_I^{Φ} [113, 312]

In (4.34), A_i is the partial molar area of species i and ξ_i is the partial molar Helmholz energy of species i in the interface. Further treatment assuming the constant value of σ leads to the expressions

$$\frac{X_I^{\Phi}}{\left(X_M^{\Phi}\right)^{A_I/A_M}} = \frac{X_I}{\left(X_M\right)^{A_I/A_M}} \exp\left(-\frac{\Delta G_I^0 + \Delta G_I^{\mathrm{E}}}{RT}\right) \tag{4.35}$$

and

$$\Delta G_I^{\mathrm{E}} = RT\left(\ln\frac{\gamma_I^{\Phi}}{\gamma_I} - \frac{A_I}{A_M}\ln\frac{\gamma_M^{\Phi}}{\gamma_M}\right). \tag{4.36}$$

Since the values of partial molar areas are known only rarely, it is usually assumed that $A_I = A_M$, and then, (4.32) and (4.26) are obtained. This approach seems to accept too many assumptions to obtain the same result as the former derivation based on the treatment of the Gibbs energy. The former derivation is thus thermodynamically clearer; we only have to keep in mind that the grain boundary energy contribution is involved in corresponding values of the standard chemical potentials.

It is evident from (4.28) that the chemical potentials of both the solute and the solvent have to be considered in the description of thermodynamic equilibrium. Therefore, the description of solute segregation analogous to the condition for phase transformations, that is considering only the chemical potentials of the solutes ($\mu_I^{\text{bulk}} = \mu_I^{\Phi}$, e.g. [315, 317]) is incorrect, and can provide misleading results. We must keep in mind that the grain boundary does not represent "a different phase" but only the defect of the crystal lattice. This is also reflected by the fact that the Gibbs energy of the grain boundary concentration dependence is higher in the whole concentration range than that of the bulk. This is also compatible with the approach of John Cahn (cf. Chap. 2) [13, 103].

Let us mention that one can meet different notation in literature that can bring extended confusion. Sometimes the Zangwill approach [318] is referred in literature considering the formal separation of the total Gibbs energy of segregation, $\Delta G = \left(\mu_I^{\Phi} - \mu_I^{B}\right) - \left(\mu_M^{\Phi} - \mu_M^{B}\right)$, which is entirely equal to zero in equilibrium (cf. (4.28)), into two parts, *configurational* and *remaining* ones. Frequently, however, another terminology is used for these two terms (e.g. [303, 319]), the *ideal* term, $\Delta G^{\text{id}} = -T\Delta S^{\text{id}} = -RT\ln\left(X_I^{\Phi} X_M / X_M^{\Phi} X_I\right)$, and an "*excess*" term, ΔG^{xs},

$$\Delta G = \Delta G^{\text{id}} + \Delta G^{\text{xs}}. \tag{4.37}$$

Then – for a binary system – we can write

$$\frac{X_I^{\Phi}}{1 - X_I^{\Phi}} = \frac{X_I}{1 - X_I} \exp\left(-\frac{\Delta G^{\text{xs}}}{RT}\right) \tag{4.38}$$

or – supposing that not each grain boundary site is available for segregation and thus, a saturation $X^{0\Phi}$ of the boundary occurs [308],

$$\frac{X_I^{\Phi}}{X^{0\Phi} - X_I^{\Phi}} = \frac{X_I}{1 - X_I} \exp\left(-\frac{\Delta G^{\text{xs}}}{RT}\right). \tag{4.39}$$

It is evident from comparison of (4.32) and (4.38) that

$$\Delta G^{\text{xs}} = \Delta G_I^0 + \Delta G_I^{\text{E}} = \Delta G_I, \tag{4.40}$$

where two "excess" terms, ΔG^{xs} and ΔG_I^{E}, appear.

It is obvious from the above considerations that the excess term ΔG_I^{E} appearing in (4.32) and (4.33) describes the *deviations between ideal and real behaviour* of any thermodynamic system. The adjective excess in this sense was introduced at beginning of the twentieth century and its usage was made common by the famous book of Lewis and Randall [304] published originally in 1923. For example, the Gibbs energy of mixing of a system is defined as $\Delta_{\text{m}}G = \Delta_{\text{m}}G^{*} + \Delta_{\text{m}}G^{\text{E}}$. It means that $\Delta_{\text{m}}G$ is composed of two contributions, the ideal Gibbs energy of mixing, $\Delta_{\text{m}}G^{*} = RT\Sigma_i X_i \ln X_i$, and the excess Gibbs energy of mixing, $\Delta_{\text{m}}G^{\text{E}} = RT\Sigma_i X_i \ln \gamma_i$ [302]. This elegant approach was chosen to conserve all relationships, which were originally derived for ideal systems, if the concentration (atom fraction) X_i is replaced by the activity, a_i, (4.31) in real systems. It is fully and systematically implemented in thermodynamics and has been successfully used for many decades (e.g. [104,303,320,321]). The adjective excess characterising the difference between the real and ideal behaviour is well established and expresses the well-defined addition to the ideal thermodynamic state function to yield the total function (Gibbs energy, internal energy, enthalpy, entropy or volume) of the real state. The term excess thermodynamic function has no other additional adjective and thus, the adjective excess represents its necessary and sufficient specification. This term was introduced at first to thermodynamic terminology without causing any controversy.

The idea of dividing ΔG into two parts in a different way, as indicated in (4.37), is principally understandable but resulted into a controversy with the above-mentioned common thermodynamic terminology. The term ΔG^{id} might be thought as "ideal", since it consists of the atomic fractions. However, the "excess" term $\Delta G^{\mathrm{xs}} = \Delta G_I$ contains both the term $-RT \ln \left(\gamma_I^{\Phi} \gamma_M / \gamma_M^{\Phi} \gamma_I\right)$, which is equal to ΔG_I^{E} (4.33), and also the term ΔG_I^0, which itself is ideal because it is a combination of the standard chemical potentials (4.22). Due to the presence of the latter contribution, ΔG^{xs} is not the "excess" term in the sense of the discussion in the preceding paragraph, and the original Zangwill proposal [318] to call ΔG^{xs} "remaining" term is more cautious.

The usage of the term "excess" for the Gibbs energy of interfacial segregation (4.40) has probably further roots. In surface physics, the adjective "excess" was introduced to denote the surface or interfacial contribution to the thermodynamic state function Y^{s} as compared to the bulk [303]. When considering an interface between two phases in a hypothetical system, the thermodynamic function Y^{s} (internal energy, entropy, ...) referring to a surface or interface s is defined as

$$Y^{\mathrm{s}} = Y - Y' - Y'', \tag{4.41}$$

where Y is the "property (function) characterising the real system" [12,303], Y' and Y'' are the functions of the phases $'$ and $''$, respectively. The thermodynamic functions Y^{s} are generally called surface or interfacial excess properties (i.e. functions) (e.g. [12, 303]) "that is we assign to the interface any excess of the thermodynamic functions of the real system over those of the hypothetical system" [303]. Besides these functions, so-called "excess" quantities (i.e. functions) per unit area of the surface/interface are often used, which are marked Y^{xs} (e.g. [303, 319]). As we have seen in the above discussion, this terminology is sometimes also used to specify characteristic thermodynamic functions of segregation, the Gibbs energy, ΔG^{xs}, the enthalpy, ΔH^{xs} and the entropy, ΔH^{xs} [303, 319].

The terminology using the complex adjective "surface/interfacial excess" is relatively new since it has never been used in surface or interfacial terminology before McLean [19], and Gleiter and Chalmers [21], and probably also not before John Cahn [102]. The adjective "excess" in the sense of characterising the surface and interfacial functions is a completely redundant over-determination because the term "surface/interfacial" itself already suggests a characteristic difference of a thermodynamic function from that of the bulk. It was introduced inconsistently without considering the established meaning of the adjective "excess" in the thermodynamics of solutions and paves the way to misunderstanding and misinterpretation. Based on the above-mentioned arguments, there is no reason to use the term "excess" to additionally characterise thermodynamic state functions for surfaces and interfaces. To avoid any confusion, it is recommended to use the simple and sufficient term *surface/interfacial thermodynamic function* to characterise the properties of the surfaces and interfaces Y^{s} (4.41), as used by Lewis and Randall [304], and to use the adjective *excess* exclusively to describe the differences between real and ideal behaviour [113].

4.3.1 Physical Meaning of Thermodynamic State Functions Appearing in Segregation Isotherms

Due to the above-mentioned ambiguity in the thermodynamic terminology of interfaces, severe misunderstanding sometimes exists in the use and interpretation of the thermodynamic state functions of segregation (cf. [113, 303, 322, 323]). Therefore, it is necessary to point out clearly the physical meaning of individual types of Gibbs energy appearing in the segregation isotherms of the Langmuir–McLean type [(4.29), (4.32), (4.35) and (4.38)] (a) the Gibbs energy of segregation, ΔG_I; (b) the standard Gibbs energy of segregation, ΔG_I^0; (c) the excess Gibbs energy of segregation, ΔG_I^{E}, and their enthalpy and entropy counterparts, as well as (d) their averaged effective functions.

4.3.1.1 Gibbs Energy, Enthalpy and Entropy of Interfacial Segregation

The physical meaning of the *Gibbs energy of interfacial segregation*, ΔG_I, of the solute I in the system $M{-}I$, that is considered as molar to preserve its intensive character, results from the definition given by (4.38) and (4.40). There is no doubt that ΔG_I completely determines the atomic fraction of the solute I at the interface (site) Φ, X_I^{Φ}, at a given temperature T and a given system composition X_I. As schematically shown in Fig. 4.2a, at constant temperature the value of ΔG_I principally changes with changing bulk composition X_I and thus with changing interfacial composition X_I^{Φ} due to mutual interaction of the species in bulk and/or interface. The corresponding enthalpy, ΔH_I, and entropy, ΔS_I, of segregation are related to ΔG_I in sense of the basic definition [101, 104, 304, 321]

$$G = H - TS. \tag{4.42}$$

It is obvious that ΔH_I and ΔS_I are identical to ΔH^{xs} and ΔS^{xs} (or sometimes also to ΔH_{seg} and ΔS_{seg}, cf. [303]), respectively, which are frequently used in the literature [319]. There is no doubt that ΔH_I and ΔS_I depend on temperature and on concentration as is obvious from many theoretical approaches. For example, the

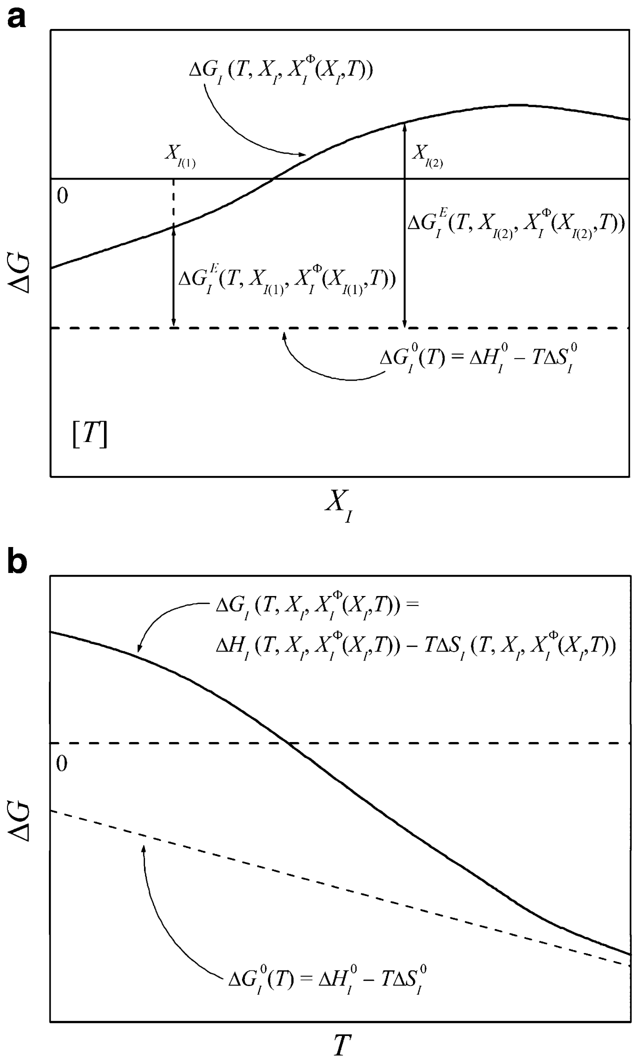

Fig. 4.2 Schematic representation of individual types of the Gibbs energy of grain boundary segregation in a binary system appearing in (4.40) in dependence on (**a**) bulk concentration, (**b**) temperature. According to (4.40), an enrichment of the interface by the solute I occurs at the bulk concentration $X_{I(1)}$ but the same interface is depleted by I at $X_{I(2)}$. When the bulk concentration of I is that specified by the value of $\Delta G_I = 0$, interfacial concentration of I is identical with its bulk concentration. See the text for the meaning of individual types of the Gibbs energy of segregation [113]

famous model of Wynblatt and Ku [303, 324, 325] gives for ΔH_I

$$\begin{aligned}\Delta H_I = &(\sigma_I - \sigma_M)A^\Phi + 2\omega\left[z^{\text{lat}}\left(X_I - X_I^\Phi\right) + z^v(X - 0.5)\right]\\ &- \frac{24\pi K_I G_M r_I (r_M - r_I)^2}{3K_I r_I + 4G_m r_M},\end{aligned} \tag{4.43}$$

where σ_i is the interfacial energy of the pure component i ($i = I, M$), A^Φ is the molar area of the monolayer interface, ω is the regular solution parameter for the $M-I$ solution, z^{lat} and z^v are the in-plane and out-of-plane co-ordination numbers, respectively, X_I and X_I^Φ are the atom fractions of I in bulk and at the interface, respectively, K_I is the bulk modulus of the solute, G_M is the shear modulus of the solvent (note that both are temperature dependent) and r_i are the atomic radii of the pure solute I and solvent M atoms [303].

Another formula for the Gibbs energy of segregation (also here inaccurately called "excess") was derived on the basis of the mean-field theory by Rabkin [326].

Segregation in real systems is affected by mutual interaction of solute and solvent atoms and by presence of third elements. Under some circumstances, interfacial depletion of the solute can be observed instead of enrichment [327]. In fact, each point in the $T-X_I$ space can be characterised by different values of ΔG_I (ΔH_I, ΔS_I) as partially visualised in Fig. 4.2. These values describe the actual segregation at the boundary (boundary site) at a fixed point on the line drawn in Fig. 4.2a and change from one state (1) to another one (2). Because each change of temperature in turn changes X_I^Φ and thus changes both ΔH_I and ΔS_I, these values can hardly be attributed to any general information, for example about the nature of the grain boundary and the anisotropy of the grain boundary segregation, because any orientation dependence of ΔH_I and ΔS_I varies in a complex way with temperature and composition, an example of which is shown in Fig. 4.3.

4.3.1.2 Standard Thermodynamic Functions of Interfacial Segregation

The *standard (molar) Gibbs energy of interfacial segregation*, ΔG_I^0, is defined as combination of the standard chemical potentials of the elements I and M at the grain boundary Φ and in the bulk according to (4.30). The chemical potentials related to the pure solute I, $\mu_{I(M)}^{0,\Phi}$ and $\mu_{I(M)}^0$, correspond to the standard states of the pure solute I at a chosen temperature and pressure of the system but in the structure of the host material M, in both bulk and interface, respectively. Note that the composition dependence of G for the bulk and the interface will be different when we exchange the meaning of M and I, that is when I will be considered as solvent and M as solute (cf. Fig. 4.1). It clearly follows from (4.30) that ΔG_I^0 (and consequently the corresponding ΔH_I^0 and ΔS_I^0) are principally independent of concentration (see Figs. 4.1 and 4.2a). In other words, $\Delta G_I^0 = \Delta G_I$ exclusively when the activity coefficients of all components are $\gamma_I = 1$, that is when $\Delta G_I^{\text{E}} = 0$ [(4.32) and (4.33)], that is in an ideal system. Despite this obviously

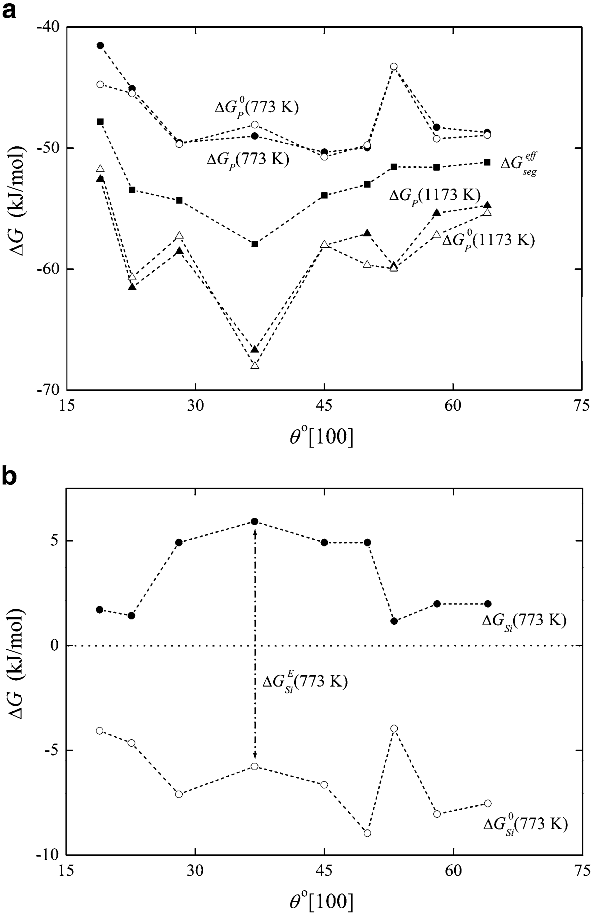

Fig. 4.3 Anisotropy of solute segregation at [100] symmetrical tilt grain boundaries in an Fe–3.55at.%Si–0.0089at.%P–0.014at.%C alloy [19] represented by orientation dependence of different thermodynamic functions. (**a**) Gibbs energies, $\Delta G_{\mathrm{P}}^{0}$ (*empty symbols*), ΔG_{P} (*solid symbols*) of phosphorus segregation at 773 K and 1,173 K. $\Delta G_{\mathrm{seg}}^{\mathrm{eff}}$ (*squares*) represents the value of $\Delta G_{\mathrm{P}}^{0}$ averaged over the same temperature range; (**b**) Gibbs energies, $\Delta G_{\mathrm{Si}}^{0}$ (*empty symbols*) and ΔG_{Si} (*solid symbols*) of silicon segregation at 773 K (the value of $\Delta G_{\mathrm{Si}}^{\mathrm{E}}$ is also shown) [113]

strong limitation, it was shown in numerous papers that many systems behave practically ideal (e.g. [328, 329]). Moreover, the ideal behaviour can be reached in an infinitesimally diluted solid solution, that is when the amount of interfacial solute enrichment is very low. Therefore, ΔG_I^0 characterises the segregation of an element I at the most advantageous site of an interface Φ in the ideal system. The standard (molar) enthalpy, ΔH_I^0, and entropy, ΔS_I^0, of interfacial segregation are defined in analogy to (4.42) and have a corresponding physical meaning.

According to (4.29), constant values of ΔG_I^0 and thus ΔH_I^0 and ΔS_I^0 define the relation between the interface activities, a_M^Φ and a_I^Φ, and the bulk activities, a_M, and a_I, of solvent M and solute I, respectively, in the whole concentration range of a binary *M–I* system (see Fig. 4.3a).

In analogy to (4.30) and (4.42), the standard molar enthalpy and entropy of segregation are given by

$$\Delta H_I^0 = \left(H_{I(M)}^{0,\Phi} - H_M^{0,\Phi}\right) - \left(H_{I(M)}^0 - H_M^0\right) \tag{4.44}$$

and

$$\Delta S_I^0 = \left(S_{I(M)}^{0,\Phi} - S_M^{0,\Phi}\right) - \left(S_{I(M)}^0 - S_M^0\right) \tag{4.45}$$

which are the respective combinations of the enthalpies and entropies[1] of the pure elements $i = I, M$, related to the interface and to the bulk. According to the choice of the standard state in which both the solute and the solvent possess identical structure of the bulk and the grain boundary at a chosen T and P, the standard thermal capacity

$$\Delta c_{p,I}^0 = \left(c_{p,I(M)}^{0,\Phi} - c_{p,I(M)}^0\right) - \left(c_{p,M}^{0,\Phi} - c_{p,M}^0\right) \equiv 0. \tag{4.46}$$

Because

$$\Delta c_{p,I}^0 = \left(\partial \Delta H_I^0 / \partial T\right) = 0 \quad \text{and} \quad \Delta c_{p,I}^0 = \left(\partial \Delta S_I^0 / \partial \ln T\right) = 0, \tag{4.47}$$

ΔH_I^0 and ΔS_I^0 are independent of temperature. This independence is *principal* property of ΔH_I^0 and ΔS_I^0: it is not the result of any averaging. This is a very important conclusion of the definition of the standard thermodynamic functions of interfacial segregation. Note that ΔH_I^0 and ΔS_I^0 substantially differ from any effective enthalpy and entropy of segregation, $\Delta H_{\text{seg}}^{\text{eff}}$ and $\Delta S_{\text{seg}}^{\text{eff}}$, the apparent temperature and/or concentration independence of which is frequently obtained by inappropriate averaging (see below).

For completeness, let us mention the pressure dependence. Correspondingly to the definition of ΔH_I^0 and ΔS_I^0 (4.44) and (4.45), the standard molar volume of segregation, ΔV_I^0,

$$\Delta V_I^0 = \left(V_{I(M)}^{0,\Phi} - V_{I(M)}^0\right) - \left(V_M^{0,\Phi} - V_M^0\right). \tag{4.48}$$

According to the choice of the standard states – pure elements I and M at the interface and/or in the bulk at the temperature, pressure and structure of the solvent M, it is evident that $V_{I(M)}^{0,\Phi} = V_M^{0,\Phi}$ and $V_{I(M)}^0 = V_M^0$, and therefore, despite (4.10), $\Delta V_I^0 \equiv 0$. Since

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[1] Note that ΔS_I^0 includes all entropy contributions of the standard states (i.e. resulting from μ_i^0), that is excluding the configuration term.

$$\left(\frac{\partial \Delta G_I^0}{\partial P}\right)_{T,n_j} = \Delta V_I^0 = 0, \tag{4.49}$$

the standard Gibbs energy of segregation is independent of pressure. Let us mention that in real systems, $\Delta V_I \neq 0$ (cf. e.g. [330]). According to definition,

$$\mathrm{d}\Delta G_I^0 = \Delta V_I^0 \mathrm{d}P - \Delta S_I^0 \mathrm{d}T + \sum_{\eta=\Phi,\nu} \sum_{i=I,M} \mu_i^\eta \mathrm{d}n_i^\eta. \tag{4.50}$$

It follows from (4.50) that

$$\left(\frac{\partial^2 \Delta G_I^0}{\partial P \partial T}\right)_{n_i} = \left(\frac{\partial \Delta V_I^0}{\partial T}\right)_{P,n_i} = -\left(\frac{\partial \Delta S_I^0}{\partial P}\right)_{T,n_i} = 0 \tag{4.51}$$

showing that ΔG_I^0 and ΔS_I^0 are independent of pressure. According to (4.42), it is evident that also ΔH_I^0 does not depend on pressure.

Let us add for completeness that the standard Gibbs and Helmholtz energies of the segregation are identical, $\Delta G_I^0 \equiv \Delta F_I^0$. This statement follows from the basic relationship between these two thermodynamic functions, $\Delta G_I^0 = \Delta F_I^0 + P\Delta V_I^0$, where $\Delta V_I^0 \equiv 0$ as shown above.

Similarly to ΔG_I^0, the standard functions ΔH_I^0 and ΔS_I^0 characterise interfacial segregation in an infinitesimally diluted binary solid solution. In this case, the interfacial solute enrichment is rather low. Due to their principal temperature, pressure and composition independence, ΔH_I^0 and ΔS_I^0 are simple but clearly defined thermodynamic functions that characterise *the tendency of the solute I to segregate at the most advantageous site of an individual grain boundary of the matrix M in an ideal system.* The actual amount of segregation at each $T{-}X_I$ state in a real system may then be simply determined from these values using the correction ΔG_I^{E} [(4.33), see below for details]. The values of ΔH_I^0 and ΔS_I^0 change exclusively with the structure of the grain boundary or grain boundary site (i.e. with the energy of the grain boundary (site)) and with the nature of the solvent and solute atoms. This is the great advantage of ΔH_I^0 and ΔS_I^0. Consequently, ΔH_I^0 and ΔS_I^0 can be used for general purposes, for example to characterise the general anisotropy of grain boundary segregation, which is directly related to the grain boundary classification scheme (see Chap. 2) [94].

4.3.1.3 Excess Thermodynamic Functions of Interfacial Segregation

According to (4.40), the excess (molar) Gibbs energy of segregation, ΔG_I^{E}, represents *the difference between the real behaviour and the ideal behaviour with respect to interfacial segregation.* ΔG_I^{E} is thermodynamically exactly defined using the activity coefficients given by (4.33). However, information about the values of the activity coefficients of the involved components in real systems is usually unknown and hardly measurable. Therefore, numerous attempts were made to find analytical expressions for this term on the basis of simplified models, which will be discussed in Sects. 4.3.3 and 4.3.4 in detail.

The role of the excess Gibbs energy of segregation, $\Delta G_I^{\mathrm{E}} = \Delta G_I - \Delta G_I^0$, as the difference between the Gibbs energy of segregation, ΔG_I, and the standard Gibbs energy of segregation, ΔG_I^0, is schematically shown in Fig. 4.2. In analogy, we can understand the physical meaning of the corresponding enthalpy and entropy terms. Figure 4.3 represents the experimental data of the orientation dependence of solute segregation of phosphorus and silicon at [100] symmetrical tilt grain boundaries in a multi-component Fe–Si–P–C-based alloy [20, 111] expressed in ΔG_I^0 and in ΔG_I. Although ΔG_I^{E} is relatively small for phosphorus segregation at [100] symmetrical tilt grain boundaries (Fig. 4.3a), a pronounced effect is evident in case of silicon (Fig. 4.3b). In fact, a high value of $\Delta G_{\mathrm{Si}}^{\mathrm{E}}$ is responsible for positive values of ΔG_{Si} for all grain boundaries at 773 K suggesting *depletion* of the interfaces by silicon in the multi-component system studied, that is caused by other, more interfacial active elements (P, C) in the alloy [20, 111]. However, the standard Gibbs energy of silicon segregation, ΔG_{Si}^0, is negative in all cases indicating that silicon principally segregates at these interfaces (when its segregation is not prevented by other solutes and/or impurities): An experimental evidence of the enrichment of the grain boundaries with silicon in pure Fe–Si-based alloys is given in [331]. As depicted in Fig. 4.3a, due to the small effect of $\Delta G_{\mathrm{P}}^{\mathrm{E}}$ on the segregation behaviour of phosphorus, the orientation dependence of both ΔG_{P}^0 and ΔG_{P} is similar, showing on the one hand, local maxima for the $\Sigma = 5,\ 36.9°[100], \{013\}$ and $53.1°[100], \{012\}$ special grain boundaries at 773 K and on the other hand, minima of ΔG_{P}^0 as well as of ΔG_P for these grain boundaries at 1,173 K. At the higher temperature, minima of ΔG_{P}^0 and ΔG_{P} were also observed at the $\Sigma = 13,\ 22.6°[100], \{015\}$ grain boundary (Fig. 4.3a). All these findings are in excellent agreement with the orientation dependence of ΔH_I^0 (see Fig. 4.4 for silicon), which is used to characterise the basic segregation behaviour of individual grain boundaries: The {015}, {013} and {012} grain boundaries in α-iron are considered as special with principally low tendency to solute segregation (singular maxima of ΔH_I^0, that is minima of the absolute values $\left|\Delta H_I^0\right|$) [94]: Actually, ΔH_I^0 is the most characteristic parameter for description of the anisotropy of grain boundary segregation (Fig. 4.4) [20]. ΔG_{Si}^0 exhibits maxima for the 36.9°[100], {013} and 53.1°[100], {012} special grain boundaries at 773 K, while ΔG_{Si} shows a minimum for the 53.1°[100], {012} but a maximum for the 36.9°[100], {013} interface (Fig. 4.3b). This result clearly indicates that the standard Gibbs energy of segregation, ΔG_I^0, reflects the classification of grain boundaries while ΔG_I does not.

4.3.1.4 Effective Thermodynamic Functions of Interfacial Segregation

Although the thermodynamic functions of interfacial segregation are clearly characterised, as reviewed above, some published experimental data (and sometimes

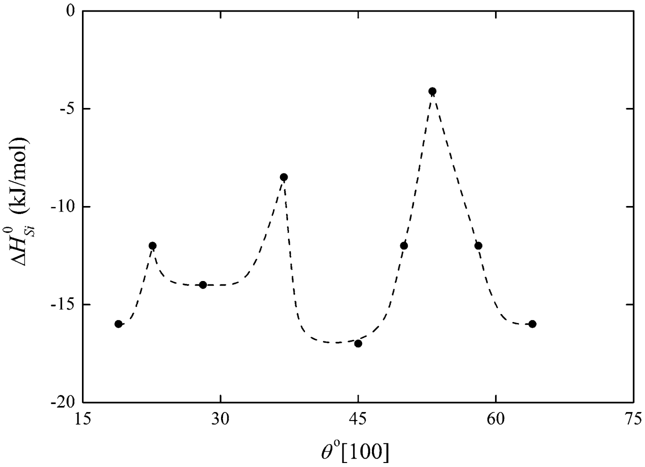

Fig. 4.4 Anisotropy of the standard enthalpy of silicon segregation in α-iron, ΔH^0_{Si}. Data from [20]

also theoretical work) are not consistent with their definitions. Data of this kind are usually obtained under additional assumptions (sometimes insufficiently specified or even not specified at all) and represent averages of one of the above-mentioned types of the Gibbs energy (enthalpy, entropy) of interfacial segregation. These data may be called *effective* Gibbs energy, enthalpy and entropy of segregation, $\Delta G^{\mathrm{eff}}_{\mathrm{seg}}$, $\Delta H^{\mathrm{eff}}_{\mathrm{seg}}$ and $\Delta S^{\mathrm{eff}}_{\mathrm{seg}}$ [113, 303].

There are several ways of averaging the data to obtain effective thermodynamic functions of interfacial segregation:

1. Determination of $\Delta G^{\mathrm{eff}}_{\mathrm{seg}}$ from the averaged chemical composition of the interfaces (i.e. neglecting the spatial distribution of segregated species) according to the segregation isotherms [(4.32) and (4.34)]
2. Averaging the values of ΔG_I for differently concentrated alloys of the same system using the ideal approximation for real systems
3. Averaging the values of ΔG_I (ΔH_I or ΔS_I) or ΔG^0_I over a temperature range (i.e. neglecting the entropy term)
4. Averaging the values of ΔG_I or ΔG^0_I over various interfaces/sites (i.e. neglecting the anisotropy of interfacial segregation)

All the above-listed types result in averaging the values of segregation enthalpy and entropy, thus providing effective functions, $\Delta H^{\mathrm{eff}}_{\mathrm{seg}}$ and $\Delta S^{\mathrm{eff}}_{\mathrm{seg}}$ [303]. It is obvious that – due to the randomly chosen averaging (cf. Fig. 4.5) – all these thermodynamic parameters have no clear physical meaning as has been frequently emphasised in literature [113, 303, 332]. Owing to this averaging, these ill-defined thermodynamic functions apparently possess similar properties as the standard thermodynamic functions ΔH^0_I and ΔS^0_I – especially the independence of concentration and/or

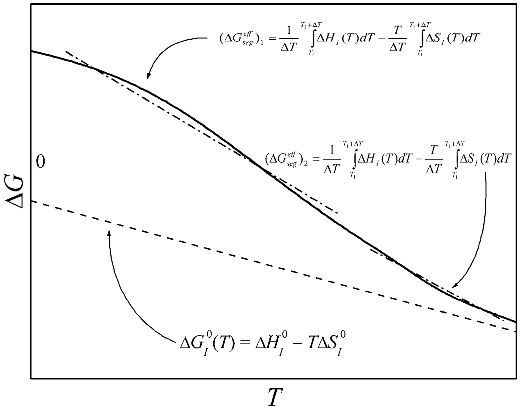

Fig. 4.5 Schematic comparison of the standard Gibbs energy of segregation, and effective Gibbs energy of segregation showing apparently similar behaviour (i.e. apparently constant $\Delta H^{\text{eff}}_{\text{seg}}$ and $\Delta S^{\text{eff}}_{\text{seg}}$) but obviously their different values

temperature. Because of this apparent but artificial similarity, these two different types of thermodynamic functions are sometimes used in place of each other and, therefore, they are misinterpreted. The main differences between the effective and standard Gibbs energies, enthalpies and entropies of segregation are discussed in the following according to the above-mentioned items.

1. *Determination of $\Delta G^{\text{eff}}_{\text{seg}}$ from averaged chemical composition of the interfaces (i.e. neglecting the spatial distribution of segregated species) according to the segregation isotherms* [(4.32) and (4.38)]. This problem of averaging is closely connected with the way of obtaining the experimental data on grain boundary concentration. As discussed in Chap. 3, the experimental data can be basically obtained in two major ways according to the analytical tools employed, namely by means of (a) microscopic techniques and (b) surface analysis techniques. In contrast to very localised and sensitive microscopic techniques the optimum lateral and depth resolutions (typically of about 10 nm and 1 nm, respectively) as well as the analytical sensitivity (0.1–1 at.%) in AES [119] are worse, and only allow to obtain a convolution of the chemical composition of typically the top 3–10 atomic layers at the surface, and averaged over a relatively large area ($\geq 10 \times 10\,\text{nm}^2$). When such "effective" concentrations are used automatically to determining the values of the thermodynamic functions of segregation, the above-mentioned effective values of $\Delta H^{\text{eff}}_{\text{seg}}$ and $\Delta S^{\text{eff}}_{\text{seg}}$ are obtained, which are averaged over an interface volume in which the segregation is confined. Indeed, the significance of these values is low if any at all.

However, there already exist techniques such as angle-resolved AES and XPS [333] and sputter depth profiling, which enable careful deconvolution of the data [333, 334], thus providing additional information about the extent of the segregation and its confinement to the chemical composition of the top interface layer (e.g. [111]). From such kind of data, the true values of ΔG_I (4.38) and also

$\Delta S_I = -(\partial \Delta G_I/\partial T)$ and $\Delta H_I = \Delta G_I + T\Delta S_I$ are obtained that represent the correct characterisation of each point in the $T{-}X_I$ space in agreement with the above analysis (see Fig. 4.2). With an appropriate correlation of the term, ΔG_I^{E} (see Sects. 4.3.3 and 4.3.4), it is possible to extract the values of ΔG_I^0 at individual temperatures and thus to determine the values of ΔH_I^0 and ΔS_I^0 from measurements of grain boundary segregation including relatively higher solute concentrations or even in multi-component systems [94, 111]. If the measurements of the solute segregation are performed at a single grain boundary of a bicrystal in a dilute system with low level of X_I^{Φ} and if the quantification is performed in a correct way, the values of ΔH_I^0 and ΔS_I^0 are obtained describing the segregation at the energetically most favourable site of that boundary (see above) [94,111]. The data obtained in this way are the *true* values of ΔH_I^0 and ΔS_I^0. Their values are no averages and they are principally independent of concentration and temperature.

2. *Averaging the values of ΔG_I for differently concentrated alloys of the same system (i.e. using the ideal approximation for real systems).* As mentioned above, substantial difference can exist between the values of ΔG_I and ΔG_I^0 that is related to the excess contribution, ΔG_I^{E} (4.40). In some cases, the measured experimental data are incorrectly interpreted by the authors who average the values of ΔG_I and take them for ΔG_I^0. As an example, let us address this case in a study of grain boundary segregation of antimony in iron [335]. The temperature dependence of grain boundary composition was measured in three Fe–Sb alloys containing 0.0055at.%, 0.0225at.% and 0.0414at.% of antimony. The summary data on temperature dependence were correlated by a single pair of the segregation enthalpy and entropy, $\Delta H_{\mathrm{Sb}} = -19\,\mathrm{kJ/mol}$ and $\Delta S_{\mathrm{Sb}} = +28\,\mathrm{J/(mol\,K)}$, respectively. These values differ substantially from those of phosphorus, $\Delta H_{\mathrm{P}}^0 = -34.3\,\mathrm{kJ/mol}$ and $\Delta S_{\mathrm{P}}^0 = +21.2\,\mathrm{J/(mol\,K)}$, measured by Erhart and Grabke [328]. Although antimony and phosphorus exhibit similar solid solubility in α-iron (3.3at.%Sb and 4.2at.%P), the above data suggest much lower segregation of antimony as compared to phosphorus. Based on this discrepancy, Briant [336] casts doubts on the general validity of the inverse relationship between the extent of interfacial segregation of an element and its solid solubility as proposed by Seah [138] (see also Chap. 5 [337]). However, a detailed analysis [338] of the data on antimony segregation [335] revealed that the values of the above-given enthalpy and entropy of segregation are $\Delta H_{\mathrm{seg}}^{\mathrm{eff}}$ and $\Delta S_{\mathrm{seg}}^{\mathrm{eff}}$, because the grain boundary composition of each Fe–Sb alloy exhibits its own temperature dependence (see Fig. 4.6a). To determine the values of ΔH_{Sb}^0 and ΔS_{Sb}^0 that do not depend on concentration and temperature, a limited amount of the grain boundary sites has to be taken into account. That means $X^{0\Phi} < 1$ in (4.39). As seen in Fig. 4.6b, the re-evaluation of the experimental data using the value $X^{0\Phi} = 0.27$ as the best-fit [338] provides an optimum correlation of original data [335]. The corresponding values of the standard enthalpy and entropy of grain boundary segregation of antimony are then $\Delta H_{\mathrm{Sb}}^0 = -23\,\mathrm{kJ/mol}$ and $\Delta S_{\mathrm{Sb}}^0 = +37\,\mathrm{J/(mol\,K)}$ [338].

With the above correction, the value of ΔH_{Sb}^0 is closer to ΔH_{P}^0 although quantitative agreement is still not good enough. However, we have to consider that AES

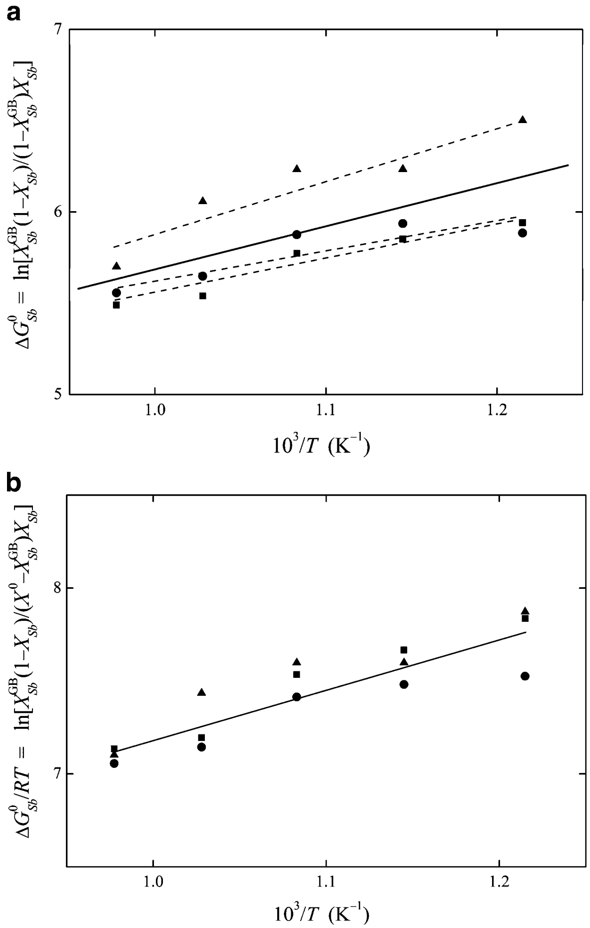

Fig. 4.6 Plot of experimental data on grain boundary segregation of antimony in polycrystalline bcc iron. Bulk concentration of antimony: 0.0055at.%Sb (triangles), 0.0225at.%Sb (circles), 0.0431at.%Sb (squares). (**a**) original data [335] correlated (*solid line*) with $X^0 = 1$, (**b**) re-evaluated data using $X^0 = 0.27$ showing independence of ΔG^0_I of bulk concentration [338]

measurements were done at Fe–Sb polycrystals with unknown character of the fractured grain boundaries (see below): If the fracture surface contains a substantial part of special interfaces (see Chap. 2), the value of ΔH^0_{Sb} reflects this fact and its absolute value is reduced as compared to the case where only general grain boundaries are present on the fracture surface. (Frankly speaking, they also represent the effective values...) The good fit of the pair ΔH^0_{Sb} and ΔS^0_{Sb} in the compensation effect (see Chap. 5) supports the assumption of a considerable amount of special interfaces in the experiment [335]. This result substantially weakens the Briant arguments [336] against the inverse relationship between the strength of interfacial segregation and the bulk solid solubility.

3. *Averaging the values of $\Delta G_I(\Delta H_I$ or $\Delta S_I)$ or ΔG_I^0 over a temperature range (i.e. neglecting the entropy term).* In some papers, the values of ΔH_I and ΔS_I or even the values of ΔG_I are averaged as [113]

$$\Delta G_{\text{seg}}^{\text{eff}} = \frac{1}{\Delta T} \int\limits_{T}^{T+\Delta T} \Delta G^{\text{xs}}(T)\text{d}T = \text{const.} \tag{4.52}$$

This averaging strongly simplifies the application of the segregation isotherms because single constant parameters are used to determine the chemical composition of interfaces at different temperatures. However, the resulting values of the effective thermodynamic functions of segregation have no physical meaning. If the Gibbs energy is averaged, the result should be considered to be the effective enthalpy of segregation, because the segregation entropy is completely neglected. For example, the segregation of phosphorus [339, 340], carbon [339], as well as silicon [340] in α-iron was evaluated in this way. As seen in Fig. 4.3a, the value of $\Delta G_{\text{seg}}^{\text{eff}}$ for phosphorus, averaged over the temperature range 773–1,173 K differs substantially from the values of ΔG_{P}^0 and ΔG_{P}. Let us repeat that in general, ΔH_I and ΔS_I depend on temperature and concentration. To overcome this complication, some authors average ΔH_I and ΔS_I over temperature (e.g. [341]) and/or concentration ranges in various ways analogously to $\Delta G_{\text{seg}}^{\text{eff}}$ in (4.52). Then, the segregation isotherm (4.32) for a binary system transforms into

$$\frac{X_I^{\Phi}}{1 - X_I^{\Phi}} = \frac{X_I}{1 - X_I} \exp\left(-\frac{\Delta H_{\text{seg}}^{\text{eff}} - T\Delta S_{\text{seg}}^{\text{eff}}}{RT}\right). \tag{4.53}$$

It is clear that the effective values of $\Delta H_{\text{seg}}^{\text{eff}}$ and $\Delta S_{\text{seg}}^{\text{eff}}$ are physically meaningless [113, 303] and (4.53) only represent an empirical correlation of the data. Nevertheless, their constant values are apparently similar to those of ΔH_I^0 and ΔS_I^0 although a fundamental difference exists between these two pairs of the thermodynamic functions as is clearly seen from their schematic comparison in Fig. 4.5. Despite this fact, these functions are sometimes misinterpreted. This is the important misunderstanding, which appears in literature (cf. [303]).

4. *Averaging the values of ΔG_I or ΔG_I^0 over various interfaces/sites (i.e. neglecting anisotropy of interfacial segregation).* Frequently, the averaging of the values of ΔG_I or ΔG^0 over numerous (usually non-specified) interfaces is applied, because many thermodynamic data on grain boundary segregation are extracted from AES measurements on polycrystalline samples (cf. [342]). In this case, the composition of different grain boundaries is measured in different samples at different temperatures, and the values of the segregation enthalpy and entropy (although considered as ΔH_I^0 and ΔS_I^0) cannot be ascribed to a single grain boundary or even site.

Let us briefly analyse the relation between the true values of the standard enthalpy and entropy with their effective counterparts. In a polycrystalline aggregate, we can express the segregation to each grain boundary in analogy to (4.32) in the simplest case of the binary ideal system as

$$\frac{X_{Ik}^{\Phi}}{X_{Mk}^{\Phi}} = \frac{X_I}{X_M}\exp\left(-\frac{\Delta G_{Ik}^0}{RT}\right), \tag{4.54}$$

where index k denotes the particular grain boundary. For the averaged composition, $X_{I,\mathrm{eff}}^{\Phi}$, over all measured grain boundaries, we can write

$$\frac{X_{I,\mathrm{eff}}^{\Phi}}{X_{M,\mathrm{eff}}^{\Phi}} = \frac{\sum\limits_{k=1}^{m} X_{Ik}^{\Phi}}{\sum\limits_{k=1}^{m} X_{Mk}^{\Phi}} = \frac{X_I}{X_M}\exp\left(-\frac{\Delta G_{I,\mathrm{eff}}^0}{RT}\right) \tag{4.55}$$

with the effective Gibbs energy of segregation, $\Delta G_{I,\mathrm{eff}}^0$. We can write (4.55) as

$$\Delta G_{Ik}^0 = -RT\ln\frac{X_{Ik}^{\Phi}}{X_{Mk}^{\Phi}} + RT\ln\frac{X_I}{X_M}. \tag{4.56}$$

Then

$$\Delta G_{I,\mathrm{eff}}^0 = -RT\ln\frac{X_{I,\mathrm{eff}}^{\Phi}}{X_{M,\mathrm{eff}}^{\Phi}} + RT\ln\frac{X_I}{X_M}. \tag{4.57}$$

In (4.57),

$$\frac{X_{I,\mathrm{eff}}^{\Phi}}{X_{M,\mathrm{eff}}^{\Phi}} = \frac{\prod\limits_{k=1}^{m} X_{Ik}^{\Phi}}{\prod\limits_{k=1}^{m} X_{Mk}^{\Phi}} = \frac{X_I}{X_M}\exp\left(-\frac{\Delta G_{I,\mathrm{eff}}^0}{RT}\right). \tag{4.58}$$

To get the single value of $\Delta G_{I,\mathrm{eff}}^0$, (4.55) and (4.58) should be identical. This condition is only fulfilled when the arithmetic and geometric averages of the interfacial concentrations over the studied grain boundaries are identical. It occurs when (a) a single grain boundary (in a bicrystal) is measured, or (b) the grain boundaries have identical composition and, consequently, are characterised by single value (or very close values) of ΔG_{Ik}^0 for all k [342]. The latter condition seems to be rather restrictive. Nevertheless, it can be approximately met even in polycrystalline materials when studying fracture surfaces with, for example AES. Because in general, decohesion is increasing with the amount of interfacial solute enrichment, it is most probable that the highly enriched general grain boundaries are opened during the fracture. The segregation levels at these boundaries at a particular temperature are very similar and their values of ΔG_{Ik}^0 (ΔH_{Ik}^0 and ΔS_{Ik}^0) are close to each other (e.g. [94]). Therefore, the thermodynamic functions obtained from AES measurements on polycrystalline samples, which are definitely of effective character, can serve as a rough estimate of the standard enthalpy and entropy of segregation at the general grain boundaries. Nevertheless, it is necessary to keep in mind all the assumptions leading to this conclusion.

A final critical remark seems to be necessary for this section. In a few publications, the data for ΔG_I, ΔH_I and ΔS_I are replaced by temperature and concentration independent "effective" values (e.g. [335,339,343,344]), here denoted as $\Delta G_{\mathrm{seg}}^{\mathrm{eff}}$, $\Delta H_{\mathrm{seg}}^{\mathrm{eff}}$ and $\Delta S_{\mathrm{seg}}^{\mathrm{eff}}$ (cf. [303]). Because their derivation is based on generally wrong assumptions or illicit simplifications, the effective values have no physical meaning as correctly pointed out in [303]. Fortunately, many of the published data on segregation represent the well-defined thermodynamic standard functions of interfacial segregation, ΔG_I^0, ΔH_I^0 and ΔS_I^0. The standard enthalpy, ΔH_I^0, and entropy, ΔS_I^0, of solute segregation are *principally* independent of temperature and concentration. The reader should pay attention to the real meaning of each set of published thermodynamic data on interfacial segregation and let us repeat it here again, should not mistake the fundamental thermodynamic standard functions ΔH_I^0 and ΔS_I^0 for the meaningless $\Delta H_{\mathrm{seg}}^{\mathrm{eff}}$ and $\Delta S_{\mathrm{seg}}^{\mathrm{eff}}$ with apparently similar properties (i.e. concentration and temperature independence, artificially obtained by averaging). An obvious lack of distinction between these two types of thermodynamic functions led some authors to the recommendation that any constant (i.e. temperature and concentration independent) values of segregation enthalpy and entropy should be avoided in interpreting measurements of anisotropy of interfacial segregation because of missing physical significance (e.g. [303]). This erroneous conclusion has to be principally rejected. During the past 20 years, careful experimental work resulted in numerous publications on anisotropy of interfacial segregation based on cautiously determined values of thermodynamic standard state functions of segregation, ΔH_I^0 and ΔS_I^0 (e.g. [20,94,111]).

4.3.2 Langmuir–McLean Model

The original derivation of the simplest form of the segregation isotherm was made by McLean [19]. In his classical approach, C solute atoms are distributed randomly among N lattice sites and c solute atoms are also randomly distributed among n independent grain boundary substitution sites. The internal energy U of this binary ideal system containing the solute atoms is [138]

$$U = cu_1 + CU_1 - kT\left[\ln n!N! - \ln(n-c)!c!(N-C)!C!\right], \tag{4.59}$$

where U_1 and u_1 are the internal energies of the solute atom in the lattice and in the grain boundary, respectively, and k is the Boltzman constant. The term at the end of the right-hand side of (4.59) is related to the configurational entropy of the random arrangement of the solute atoms in the bulk and grain boundary. The equilibrium state of the system occurs at the minimum value of U. This may be determined by differentiating U with respect to c, noting that the sum of $c + C$ remains constant. The grain boundary analogue of the Langmuir adsorption to the free surfaces is obtained,

$$\frac{X^{\Phi}}{1 - X^{\Phi}} = \frac{X}{1 - X} \exp\left(-\frac{\Delta u}{kT}\right). \tag{4.60}$$

In (4.60), it is supposed that $c \ll n$ and $C \ll N$. Then $X^{\Phi} = c/n$ and $X = C/N$. $\Delta u = u_1 - U_1$ is the molar internal energy of segregation. Let us stress out that according to (4.60), the segregation is driven by changes of the internal energy while in the binary real analogue, (4.32), this term is replaced by the Gibbs energy of segregation. It means that in (4.60), all entropy contributions such as anharmonic, vibration, etc. are neglected except the configurational entropy, $k \ln[(X^{\Phi}(1 - X))/(X(1 - X^{\Phi}))]$, which is used for determination of the grain boundary composition. From this point of view, the segregation isotherm expressed by (4.32) is more general, because it was derived without any additional assumption concerning the distribution of the species in the system. Equation (4.32) also considers – besides the configurational term – other contributions to the segregation entropy, which were shown in many cases to play an important role in grain boundary segregation [20,94,327,341,345].

Equation (4.60) is the well-known Langmuir–McLean segregation isotherm. In its derivation it is assumed that all grain boundary positions are substitution sites and are available for segregation. In some cases, only a submonolayer fraction may be available for grain boundary segregation in saturation. As shown by Hondros and Seah [308], the Langmuir–McLean isotherm should be rewritten as

$$\frac{X_i^{\Phi}}{X^{0\Phi} - X_i^{\Phi}} = \frac{X_i}{1 - X_i} \exp\left(-\frac{\Delta g}{kT}\right) \tag{4.61}$$

where the internal energy of segregation was already replaced by corresponding Gibbs energy. The same result can be obtained from (4.32) and (4.33) supposing a binary system ($X_I = 1 - X_M$) with ideal behaviour ($X_i = a_i$, i.e. $\gamma_i = 1$ and thus $\Delta \overline{G}_I^{\mathrm{E}} = 0$) and considering the saturation limit $X^{0\Phi}$. For example, the average saturation level, $X^{0\Phi}$, of grain boundaries in copper for antimony segregation was found to vary between 0.38 and 0.65 of Sb monolayer [346] and 0.27 for segregation of antimony in bcc iron [338]. The Langmuir–McLean segregation isotherm was successfully applied to the description of the equilibrium composition of the grain boundaries in a spectrum of binary systems such as bcc iron with molybdenum and niobium [231].

Besides the substitutional sites, however, the grain boundary also contains interstitial sites. These sites can be understood as the sites, which cannot be occupied by the matrix atoms in equilibrium but may accept the atoms of other solutes. Due to the atomic structure of these interfaces, the free volume among equilibrium atom positions is large enough to accept – besides typical interstitial atoms – even much larger atoms that occupy the substitutional sites in regular crystal lattice. For example, phosphorus, tin and antimony in bcc iron and bismuth in copper are substitutional solutes, however, they segregate at interstitial positions. To describe the interstitial segregation, we will assume that the boundary in a binary system is composed of two sublattices. The "substitution" sublattice is completely filled by the atoms of the base element. The interstitial positions in matrix material, $M_\square$, are partially filled by the atoms of the solute I so that there occurs an exchange $I + M_\square^\Phi \leftrightarrow I^\Phi + M_\square$. Defining the chemical potentials and activities for individual components including the unoccupied interstitial positions $M_\square$ in both, the grain boundary and the bulk, we can write an expression principally analogous to (4.29),

$$\frac{a_I^\Phi}{a_{M_\square}^\Phi} = \frac{a_I}{a_{M_\square}} \exp\left(-\frac{\Delta G_I^0}{RT}\right). \tag{4.62}$$

In this case, ΔG_I^0 the standard molar Gibbs energy of segregation is defined as $\Delta G_I^0 = \left(\mu_I^{0,\Phi} + \mu_{M_\square}^0\right) - \left(\mu_I^0 + \mu_{M_\square}^{0,\Phi}\right)$. $\mu_{M_\square}^{0,\Phi}$ and $\mu_{M_\square}^0$ are the respective chemical potentials of the grain boundary vacancies $M_\square^\Phi$ and of the volume vacancy or substitutional atom depending on whether the solute is substitutional or interstitial in volume [347].

In case of interstitial segregation, however, not all grain boundary positions can be occupied by the solute segregating at interstitial positions: the substitutional positions in the grain boundary always remain occupied by the matrix atoms. The interstitial segregation is completed when all allowed interstitial positions are occupied by the segregated species. Thus, the "usual" segregation occurs in the interstitial sublattice,

$$\frac{\theta_I^\Phi}{\theta_{M_\square}^\Phi} = \frac{X_I}{X_{M_\square}} \exp\left(-\frac{\Delta G_I^0 + \Delta G_I^{\mathrm{E}}}{RT}\right), \tag{4.63}$$

where θ_i^Φ is the atomic concentration of segregated interstitial solute I or fraction of free interstitial positions $M_\square$ in the interstitial sublattice. θ_I^Φ is related to the total concentration at the grain boundary by

$$\theta_I^\Phi = \frac{X_I^\Phi}{X_{\mathrm{int}}^{0\Phi}} \tag{4.64}$$

with $X_{\mathrm{int}}^{0\Phi}$ being the fraction of the interstitial positions available for solute segregation at the grain boundary. We can then rewrite (4.63) as

$$\frac{X_I^\Phi}{X_{int}^{0\Phi} - X_I^\Phi} = \frac{X_I}{1 - X_I} \exp\left(-\frac{\Delta G_I^0 + \Delta G_I^{\mathrm{E}}}{RT}\right), \tag{4.65}$$

which is similar to the Hondros and Seah formulation of the segregation isotherm (4.61) [173, 308] supposing $\Delta G_I^{\mathrm{E}} = 0$ (i.e. ideal behaviour) [316].

To describe the grain boundary segregation rigorously in an ideal multicomponent system, (4.32) can be used with $\Delta G_I^{\mathrm{E}} = 0$,

$$\frac{X_I^{\Phi}}{1 - \sum\limits_{i=1}^{M-1} X_i^{\Phi}} = \frac{X_I}{1 - \sum\limits_{i=1}^{M-1} X_i} \exp\left(-\frac{\Delta G_I^0}{RT}\right). \tag{4.66}$$

Expression (4.66) is often used to describe so-called *site competition* of segregating solutes: The site competition effect is considered to be involved in the sum $\sum_{i=1}^{M-1} X_i^{\xi}$. The term $1 - \sum_{i=1}^{M-1} X_i^{\xi}$, however, only denotes the concentration of the matrix element at the grain boundary ($\xi = \Phi$) or in the volume. However, in some cases, the segregation of an element is unaffected by other present elements at all. This is, for example, for elements that segregate at different boundary sites (interstitial and substitution sites, see Sect. 4.3.3). Then the system is considered as "pseudobinary" and (4.60) or (4.61) can be applied to describe the concentration of the segregated impurity. Such case was found, for example for phosphorus segregation in a low-alloy steel [329]. In real systems, however, the interaction between the solute atoms may play a role and two solutes can be mutually repulsed or attracted despite they segregate at substitution or interstitial positions [348]. Sometimes, it is not easy to distinguish between repulsive interaction and site competition [349]: only in the case when the atoms of both solutes occupy different grain boundary sites (for example silicon and phosphorus), the repulsive interaction can be unambiguously proved [350]. For more details see Sects. 4.3.3 and 4.3.4.

Grain boundary "site competition" has been reported between nitrogen and sulphur in bcc iron [351] but not under all conditions [352]. The most important example of the site competition is the replacement of phosphorus by carbon at grain boundaries in bcc iron [328, 339, 353–356]. Further published examples of this phenomenon are listed in Table 4.1. However, in some cases such as Ni–C the site competition is hardly acceptable when taking into account that both elements segregate at different sites in bcc iron matrix (nickel segregates at substitutional sites while carbon at interstitial positions) [98, 375].

Langmuir–McLean segregation isotherms represent historically the first model for the description of equilibrium segregation at solid interfaces in dependence on the bulk composition and temperature. In principle, it should be successfully applied to describe the grain boundary segregation in all binary and pseudobinary systems dilute enough to exhibit ideal behaviour. It has been frequently used to characterise grain boundary segregation in such systems, for example, it was used to correlate grain boundary segregation of phosphorus [329], tin [123] and sulphur [376] in bcc iron, phosphorus, carbon and boron [344], manganese and phosphorus [377], manganese, phosphorus and boron [378] and phosphorus [379] in fcc-based iron systems including 17Cr–12Ni stainless steels, indium and sulphur in nickel [334] and platinum, palladium and rhodium in gold [380].

Table 4.1 Examples of site-competitive grain boundary segregation

Matrix	Competitively segregating elements	Reference
α-Fe	P–S	[357–361]
	P–C	[328, 339, 353, 354, 360, 362–367]
	P–N	[360, 363]
	P–B	[367]
	P–Sb	[357]
	N–C	[360]
	S–C	[351, 354, 360, 368, 369]
	S–N	[351, 360, 368]
	Sb–C	[370]
	Sn–S	[367, 371]
Mo	C–O	[130]
W	P–C	[372]
γ-Fe	P–N	[373]
Ni	P–S, Sb–S	[374]

Phosphorus is probably the most frequently examined element in respect to the grain boundary segregation in α-iron. This interest was evoked by its large embrittling potency in iron and steels. As mentioned above, the first quantitative study of the grain boundary segregation by AES was focused just on phosphorus segregation in low-alloy ferrite steels [121]. In the first thorough quantitative study of grain boundary segregation of phosphorus in α-iron, Erhart and Grabke [328] studied chemical composition of the grain boundaries in polycrystalline iron containing various volume concentrations of phosphorus ranging from 0.003 to 0.33 mass%, at temperatures between 400 and 800°C. Using the Langmuir–McLean segregation isotherm (4.60) to correlate the experimental data, they evaluated $\Delta H_{\mathrm{P}}^{0} = -34.4\,\mathrm{kJ/mol}$ and $\Delta S_{\mathrm{P}}^{0} = +21.5$ J/(mol K). Argon ion sputtering of the fracture surfaces as well as FIM studies confirmed that the segregation effects are confined in a single or merely few monatomic layers along the grain boundary [198].

Similarly to the Fe–P system, a detail study was performed to evaluate the sulphur grain boundary segregation in polycrystalline α-iron by Briant on the alloys ranging from 0.0035 to 0.013 at.%S in volume at temperatures 400, 480 and 550°C. It was shown that maximum grain boundary concentration of sulphur appears at intermediate temperature. It reflects complex effect of the segregation tendencies and strong decrease of the bulk solid solubility of sulphur with decreasing temperature. At lower temperatures, the amount of sulphur in bulk ferrite solution is substantially reduced: it reflects in the amount of this element at the grain boundaries. The enthalpy of sulphur grain boundary segregation in α-iron was determined to be $\Delta H_{\mathrm{S}}^{0} = -51.5\,\mathrm{kJ/mol}$ [381]. However, its bulk content is generally strongly suppressed by presence of manganese and thus, by precipitation of MnS resulting from strong attractive interaction [313]. Thus, the bulk concentration of sulphur in steels is so low that no extended sulphur grain boundary segregation is observed [123]. Similar example of the "scavenging" of soluble impurities in iron is the precipitation of iron oxides due to the low solubility of oxygen in iron: then the amount of soluble oxygen is too small to segregate in iron [313, 382].

Grain boundary segregation of tin was found to be saturated well below a monolayer [123], although it exhibits a large scatter of measured values. This was ascribed to the strong effect of anisotropy of grain boundary segregation (see Chap. 7). The values of the thermodynamic parameters of the grain boundary segregation were determined on basis of the Langmuir–McLean segregation isotherm, (4.66), as $\Delta H^0_{\mathrm{Sn}} = -22.5\,\mathrm{kJ/mol}$ and $\Delta S^0_{\mathrm{Sn}} = +26.1\,\mathrm{J/(mol\,K)}$ [123]. These data are in good agreement with the measurements of Seah and Hondros [307] providing the value ΔG^0_{Sn} (823 K) $= -44\,\mathrm{kJ/mol}$. However, tin exhibits large tendency to surface segregation and it is considered that this effect is responsible for temper embrittlement of low alloy steels by tin. Tin is allowed to segregate at the surfaces of the voids and cavities inside the material upon creep as well as in the intergranular crack front at intermediate temperatures during dynamic embrittlement similarly to copper-based alloys [383] (see also Chap. 7).

An interesting example of the limited sites allowed for segregation is the grain boundary chemistry in ordered intermetallics. Principally, the solutes and impurities segregate at the grain boundaries in ordered alloys in very low concentrations [127, 347, 384]. Therefore, we can well assume that the segregation level is controlled by ordering of the system and then, we can use (4.61) to describe this kind of grain boundary segregation. Similarly to free surfaces [385], grain boundaries in ordered systems may also exhibit extended or less extended ordering tendencies. Let us assume that no segregation is allowed at the completely ordered grain boundary while the segregation at the disordered parts exhibits the Langmuir–McLean behaviour. Accepting that the portion of the ordered grain boundary region can be described by the grain boundary order parameter $m^{\Phi}(T)$, the average grain boundary concentration X_I^{Φ} can be expressed as [179]

$$X_I^{\Phi}(T) = X_I^{\Phi\mathrm{D}}(T)[1 - m^{\Phi}(T)] + X_I m^{\Phi}(T), \tag{4.67}$$

where $X_I^{\Phi\mathrm{D}}$ is the grain boundary concentration of a solute I in conditions of disordered solid solution (i.e. the Langmuir–McLean behaviour). Combining (4.61) and (4.67) and introducing a general concentration

$$Y_I^{\Phi} \equiv X_I^{\Phi} - X_{Im}^{\Phi}(T), \tag{4.68}$$

we obtain

$$\frac{Y_I^{\Phi}}{X^{0\Phi} - Y_I^{\Phi}} = \frac{X_I}{1 - X_I}\exp\left(-\frac{\Delta G_I^0}{RT}\right), \tag{4.69}$$

where

$$X^{0\Phi} = 1 - m^{\Phi}(T). \tag{4.70}$$

If the product $X_i m^{\Phi}(T)$ is small in comparison to X_I^{Φ}, (4.69) transforms onto (4.61). It means that for solute segregation at partially ordered grain boundaries, $X^{0\Phi}$ is equal to the portion of the disordering of the grain boundary at a given temperature, characterised by the grain boundary order parameter $m^{\Phi}(T)$. In other words, the ordered material can be considered as a chemical compound with limited free species as well as positions available for segregation.

The parameter, $m^{\Phi}(T)$, can be evaluated according to the expression [385, 386]

$$m^{\Phi}(T) = \left(\frac{T_{\mathrm{c}}^{\Phi} - T}{T_{\mathrm{c}}^{\Phi}}\right)^{\beta^{\Phi}}, \tag{4.71}$$

where T_{c}^{Φ} is the grain boundary ordering temperature, and β^{Φ} is the grain boundary exponent. The value of β^{Φ} lies between those of the bulk, $\beta^{\mathrm{bulk}} = 0.3$, and of the surface, $\beta^{\mathrm{surface}} = 0.8$ [179, 385]. We can well suppose – considering the number of the broken bonds of the atoms in various surroundings – that β^{Φ} will possess an intermediate value, probably closer to that of the bulk. The value of the grain boundary ordering temperature, T_{c}^{Φ}, can differ from that of the bulk, T_{c} [385]. In fact, both relationships, $T_{\mathrm{c}}^{\Phi} > T_{\mathrm{c}}$ and $T_{\mathrm{c}}^{\Phi} < T_{\mathrm{c}}$ are possible. Generally, the value of T_{c}^{Φ} may change with grain boundary type and orientation. The values are expected to be closer to T_{c} in the case of special grain boundaries as compared to general ones. Since the values of T_{c}^{Φ} representing a non-clearly-defined average value over all interfaces in a polycrystal, are not known, this term represents a fitting parameter. However, it has to keep its physical meaning as the temperature: Therefore, only T_{c}^{Φ} values comprised in the range (0, T_{m}), where T_{m} is the melting temperature, are accepted.

Let us now point an interesting consequence of existence of different saturation limits. Supposing the limited number of positions for segregation, X_1^0, as described for example by (4.65), we can add a further portion of attainable positions, $X_2^{0\Phi}$, as limited by another source. Then, the left-hand side of (4.65) will change to $\theta_I^{\Phi}/\left(X_2^{\Phi} - \theta_I^{\Phi}\right)$. According to the definition of $\theta_I^{\Phi} = X_I^{\Phi}/X_1^0$ (e.g. (4.64)), we can write it as $X_I^{\Phi}/\left(X_1^{0\Phi}X_2^{0\Phi} - X_I^{\Phi}\right)$ and, in general, it results in

$$X_{\mathrm{total}}^{0\Phi} = X_1^{0\Phi} \times X_2^{0\Phi} \times \cdots \times X_k^{0\Phi} = \prod_{i=1}^{k} X_i^{0\Phi}. \tag{4.72}$$

In both the stoichiometric Ni_3Al-based intermetallics and in the Al-rich Ni_3Al, no segregation effects have been observed [387, 388]. In Ni-rich Ni_3Al alloys, boron segregation is observed accompanied probably by nickel co-segregation. Maximum reported amount of 14at.% of boron was detected at grain boundaries of a Ni–24at.%Al(0.1at.%B) alloy at 1,273 K [389]. Boron segregation in Ni-rich Ni_3Al was correlated by $\Delta H_{\mathrm{B}} = -11$ kJ/mol and $\Delta S_{\mathrm{B}} = 22$ J/(mol K) for the alloy containing 0.048 at.% of boron, while $\Delta H_{\mathrm{B}} = -10$ kJ/mol and $\Delta S_{\mathrm{B}} = 9$ J/(mol K) were found for the material with 0.48at.% of boron. In all these measurements, very low levels of boron segregation of about 1–2 at.% were found [390]. The level of enrichment of the grain boundaries in Ni–49.7at%Al–0.7at.%Mo–0.4at.%Zr did also not exceed 1.5 at.% [391]. Ni-rich Ni_3Si also exhibits boron segregation with the maximum reported level of about 5 at.% at 873 K [392].

4.3.3 Guttmann Model of Grain Boundary Segregation in Interacting Multi-component Systems

In the above description, we concentrated mainly on ideal (infinitesimally diluted) binary (pseudobinary) systems where the activities can simply be replaced by concentrations, that is where ΔG_I^{E} in (4.32) and (4.35) can be neglected. To study the grain boundary segregation at higher concentration levels, this term has to be taken into account because the activity of the solute differs from the concentration due to the solute–solute interactions. Then, the activities (activity coefficients) should be evaluated to obtain ΔG_I^0. However, this evaluation is not easy at all and therefore, various types of empirical or semi-empirical correlation are used to evaluate the excess Gibbs energy of segregation.

The most common model, which has not been overcome till now, is based on the regular solid solution according to the "zero-order quasichemical approximation". This model supposes randomly distributed solute and solvent atoms among the fixed number of equivalent sites both in the bulk and in the grain boundary and constant pair interaction energy between the nearest neighbours [313,314,320,393]. The interaction coefficients α_{ij} in a regular solution are related to the excess Gibbs energy, ΔG_I^{E}, which is equal to the enthalpy of mixing, $\Delta_m H$,

$$\Delta G_I^{\mathrm{E}} = \Delta_m H = \sum_{i<j} \alpha_{ij} X_i X_j \tag{4.73}$$

with

$$\alpha_{ij} = Z N_0 \left[\varepsilon_{ij} - \frac{\varepsilon_{ii} + \varepsilon_{jj}}{2} \right], \tag{4.74}$$

where Z is the coordination number in the crystal (boundary), N_0 is the Avogadro's number and ε_{ij} are energies of the $i - j$ bonds [393]. Combining (4.73) and (4.74) with the condition $X_M = 1 - \sum_{J=1}^{M-1} X_J$, we obtain

$$\Delta G_I^{\mathrm{E}} = -2 \left(\alpha_{IM}^{\Phi} X_I^{\Phi} - \alpha_{IM} X_I \right) + \sum_{J \neq I,M} \left(\alpha_{IJ}'^{\Phi} X_J^{\Phi} - \alpha_{IJ}' X_J \right), \tag{4.75}$$

where $\alpha'_{IJ} = \alpha_{IJ} - \alpha_{IM} - \alpha_{JM}$ is the net interaction between solutes I and J, α_{IJ}, with respect to their interactions with the matrix element M, α_{IM} and α_{JM}. Although the interaction coefficients can principally be different for the grain boundary and for the bulk due to different co-ordination numbers and atomic distances in the respective structures, the role of chemical interactions should be the same if it is assumed that $\alpha_{IJ}^{\Phi} \cong \alpha_{IJ}$ [313]. Then we can write

$$\Delta G_I^{\mathrm{E}} = -2\alpha_{IM}^{\Phi}\left(X_I^{\Phi} - X_I\right) + \sum_{J \neq I,M} \alpha_{IJ}'^{\Phi}\left(X_J^{\Phi} - X_J\right). \tag{4.76}$$

Combination of (4.32) and (4.75) or (4.76) represents the well-known form of the Guttmann type of the segregation isotherm for the case of solute segregation in non-ideal (regular) multicomponent system [313]. Let us notice that in the present notation, repulsive interaction is characterised by the values $\alpha_{IJ}'^{\Phi} > 0$ while $\alpha_{IJ}'^{\Phi} < 0$ describes attractive interaction. The interacting elements in various matrices are listed in Table 4.2.

The Guttmann model of interactive segregation in multicomponent systems was successfully used to describe the grain boundary segregation in various systems. The character of the ternary interaction was found to be repulsive for Si–P ($\alpha'_{\mathrm{SiP}} = 92$ kJ/mol) and for P–C ($\alpha'_{\mathrm{CP}} = 7$ kJ/mol), and attractive in case of Si–C ($\alpha'_{\mathrm{SiC}} = -3$ kJ/mol) pairs [111]. The strong P–Si repulsive interaction was directly

Table 4.2 Examples of interaction pairs during grain boundary segregation

Matrix	Type of interaction	Interacting elements	Reference
α-Fe	Repulsive	P–B, P–S, C–Sn	[348, 394]
		P–Si	[348, 350, 395–397]
		C–Si	[347, 349]
		Si–N	[398]
		Si–Sb	[398]
		Si–B	[241]
		P–Nb	[399]
		Sn–S	[366]
	Attractive	P–Ni, P–Mn, Sb–Mn, Sb–Cr, Sb–Mo	[348, 400]
		Sb–Ni	[348, 364, 401]
		P–Cr, P–Mo	[348, 364, 366, 402]
		Ni–Sn	[366, 367]
		C–P	[349, 351]
		V–P	[313, 363, 402]
		Sb–Ti	[355, 367]
		P–Ti	[355, 403]
		S–Mn	[404]
		S–H, C–H	[405]
		Ti–H	[406]
		Cr–N	[366]
Ir	Repulsive	Th–Si	[407]
W	Repulsive	Fe–C, Fe–O	[407]
γ-Fe	Repulsive	P–S	[408, 409]
		P–B	[410]
		P–C	[411]
		P–Mo	[412]
	Attractive	Cu–Sn, Cu–Sb	[401]
Ni	Attractive	Mo–P, Nb–P	[126]
	Repulsive	S–N	[144]

proved by scanning tunnelling microscopy at low-index free surfaces of bcc iron showing a depletion of silicon in vicinity of islands of segregated phosphorus atoms [413]. Zhang et al. showed a pronouncedly increasing repulsive interaction between phosphorus and sulphur with decreasing temperature (54 kJ/mol at 973 K while 79 kJ/mol at 773 K) [394]. Attractive interactions were detected between phosphorus and various transition metals, P–Cr ($\alpha'_{\mathrm{CrP}} = -3$ kJ/mol), P–Mo ($\alpha'_{\mathrm{MoP}} = -23$ kJ/mol) and P–V ($\alpha'_{\mathrm{VP}} = -11$ kJ/mol [394] or -144 kJ/mol [313]). Attractive interaction was also indicated for phosphorus with molybdenum and niobium in IN 718 nickel-based superalloys [127]. From strong repulsive interaction of tin and silicon on the (4.46) surface of bcc iron ($\alpha'_{\mathrm{SnSi}} = -50$ kJ/mol), it is deduced that similar repulsion will exist at the grain boundaries [414]. The finding that silicon segregates at a special grain boundary of α-iron, while boron segregates at general grain boundaries suggests repulsion between these two kinds of atoms [241].

Equation (4.76) is the simplest correlation of ΔG_I^{E} for the regular system containing the substitution atoms only (model 1). This model was extended to more complex cases supposing regular solutions of both substitution and interstitial solutes without competition (model 2), quasimolecular behaviour with site competition taking into account formation of an $I_x J_y$ compound (model 3), quasimolecular non-competitive behaviour in two distinct (substitution and interstitial) sublattices considering the formation of an $I_x J_y$ compound (model 4), and – last but not the least – formation of a two-dimensional ternary compound (model 5) [313]. These models were developed by Guttmann and McLean [313] and thoroughly discussed by Militzer and Wieting [415]. In general, the segregation equations corresponding to the models 1–5 can be displayed (by neglecting the binary interaction parameters and supposing dilute bulk solid solution) as

$$\frac{Y_I^{\Phi}}{Y_M^{\Phi}} \cong X_I \exp\left(-\frac{\Delta G_I}{RT}\right) \tag{4.77}$$

with

$$\Delta G_I = \Delta G_I^0 + \sum_{J \neq I,M} Q_{IJ} Y_J^{\Phi}, \tag{4.78}$$

where Y_I^{Φ} and Q_{IJ} are the generalised terms for interfacial concentration and ternary solute interaction, respectively. The meaning of these quantities is given in Table 4.3 for individual models.

For classical example of the mutual enhancement of grain boundary segregation of two solutes, there may serve the behaviour of nickel and antimony in bcc iron. It was found that presence of nickel increases grain boundary segregation of antimony and vice versa [349,370,393,416–418]. Guttmann et al. quantitatively interpret this kind of segregation behaviour as a consequence of an attractive interaction between the atoms of nickel and antimony [175,393,416] (Fig. 4.7). This conclusion was frequently criticised on basis of other experimental findings showing that changes in antimony concentration do not affect nickel segregation [419–422]. The main objection following from these experiments is that the effect is caused by interaction of

Table 4.3 Parameters of individual models 1–5 of grain boundary segregation in multicomponent alloys [313] [(4.77) and (4.78)]

Model	Y_I^Φ	Y_M^Φ	Q_{IJ}	Note
1	X_I^Φ	$1-\Sigma_{J\neq M}X_J^\Phi$	α'_{IJ}	
2	$\dfrac{X_I^\Phi}{1-\sum_{\text{int}}X_J^\Phi}$	$1-\dfrac{\sum_{\text{subst}\neq M}X_J-(b/c)\sum_{\text{int}}X_J^\Phi}{1-\sum_{\text{int}}X_J^\Phi}$	$b\alpha'_{IJ}$	I = subst(itutional)
			$c\alpha'_{IJ}$	J = int(erstitial)
3	X_I^Φ	$1-\Sigma_{J\neq M}X_J^\Phi$	→	Complex functions of Y_I^Φ and Y_M^Φ
4	$\dfrac{X_I^\Phi}{1-\sum_{\text{int}}X_J^\Phi}$	$1-\dfrac{\sum_{\text{subst}\neq M}X_J-(b/c)\sum_{\text{int}}X_J^\Phi}{1-\sum_{\text{int}}X_J^\Phi}$	→	Complex functions of Y_I^Φ and Y_M^Φ
5	$\dfrac{X_I^\Phi}{1-\sum_{\text{int}}X_J^\Phi}$	$1-\dfrac{\sum_{\text{subst}\neq M}X_J-(b/c)\sum_{\text{int}}X_J^\Phi}{1-\sum_{\text{int}}X_J^\Phi}$	$c\alpha'_{IJ}$	

b and c are the fractions of substitution and interstitial lattice sites, respectively ($b+c=1$)

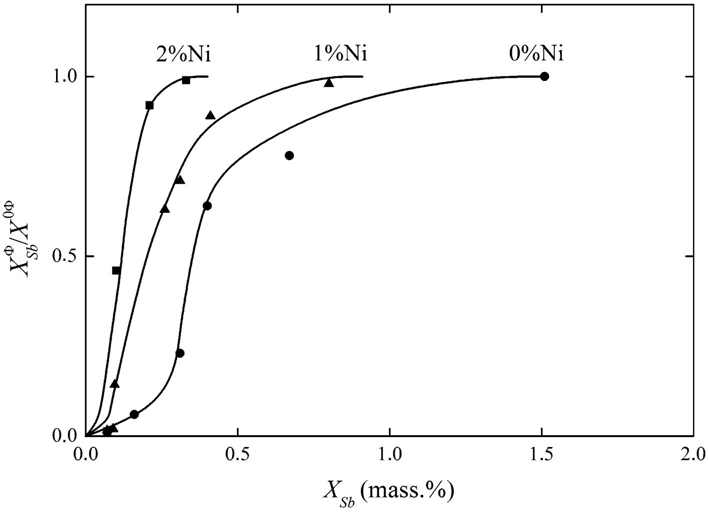

Fig. 4.7 Isotherms of the grain boundary segregation of antimony in Fe–Ni–Sb alloys as a function of the bulk antimony concentration for different content of nickel in the alloy. According to [416]

these elements with carbon as the trace impurity in the material used. Grabke and Briant proposed to explain the segregation behaviour in multicomponent systems on basis of both the changed solubility and activity of the solutes in iron due to presence of another impurity and the site competition. In the above case of the segregation in an Fe–Ni–Sb alloy, the increased segregation of antimony with increasing content of nickel is explained as reduction of the bulk concentration of carbon as an impurity in the system. Thus, carbon is less effective in site competition with antimony and, therefore, the grain boundary concentration of antimony may increase [419–422].

Table 4.4 Examples of scavenging or gettering effects influencing grain boundary segregation

Matrix	Scavenging/gettering effect	Reference
α-Fe	Fe + O → oxides	[423]
	Mn,Ca,Cr,Ce + S → sulphides	[367, 423–425]
	Fe,Ni,Mo,Nb,Ti,V,Cr,Mn + C → carbides	[363, 400, 420, 423, 424, 426]
	Mo,Nb,Ti + P → phosphides	[123, 355, 381, 400, 424, 427, 428]
	Cr,Ti,Mo + N → nitrides	[123, 408, 429, 430]
	Mn,Fe,Ni,Ti,Nb,Cr + Sb → antimonides	[422, 431]
	Ti + H → hydride	[405]
γ-Fe	Nb,Mn + S → sulphides	[432]
	Fe,Nb,Cr,Mo,Ni + C → carbides	[373, 377, 432–434]
Ir	Ir,Th + Si → silicides	[406]
Ni	Ti,Nb,Ca,Mg,Y,Zr + S → sulphides	[125, 435]
	Ti,Nb + N → nitrides	[125]
	Ti + C + N → carbidonitrides	[435, 436]
	Cr + C → carbides	[436]

This situation is rather general because carbon exerts a large tendency to precipitate as carbides with many other solutes such as molybdenum, vanadium, titanium or tantalum [349, 417, 420] (cf. Table 4.4). This fact serves as a general explanation of reduced competition with other segregating elements such as phosphorus [417]. However, the effect of site competition should be of little power in dilute alloys and the interactive segregation seems still to be the most reasonable explanation for observed behaviour [336]. Let us state that site competition and repulsive interaction do not compete each to the other: Both effects can synergistically be used to correlate the data more precisely [313, 437] as was shown, for example of phosphorus, silicon and carbon grain boundary segregation in iron [350].

Let us conclude that the segregation behaviour in a multicomponent alloy reflects various effects that should be considered in full interpretation of the data [423]. We should consider (a) the basic tendency of the solutes to segregate at the grain boundaries, (b) the changes in the bulk composition due to the scavenging and gettering effects and following precipitation, (c) the site competition and (d) the mutual interaction of different atoms. However, if we want to study the grain boundary composition in a multicomponent alloy, we should avoid all effects that are not connected with segregation. Primarily, we should only consider the true concentrations of dissolved solutes and impurities in the matrix phase that are available for segregation, and not to use the nominal composition of the system. In this way, the problems with possible scavenging and gettering do not come into discussion and the situation becomes clearer. Another effect, which should be avoided, is the saturation of the boundaries: When a boundary is saturated, fine details of co-segregation may be invisible [418]. Then, we can simply consider the changes of the activities of the system that can be correlated by various approaches (although presently, the only available approach is the interaction model of Guttmann (4.83) and (4.84) and relate the grain boundary concentration of a segregated element to the grain boundary concentration of the matrix element (site competition, (4.66)) to describe the segregation behaviour in the system under consideration. The Guttmann model may seem to be too simplified but – as already mentioned above – till now no other alternative has been proposed to describe interfacial segregation in real systems.

4.3.4 Fowler Model

In a binary system, the ternary interaction coefficients α'_{IJ} will be neglected and (4.76) reduces into

$$\Delta G_I^{\mathrm{E}} = -2\alpha_I^{\Phi}\left(X_I^{\Phi} - X_I\right). \tag{4.79}$$

Expression (4.79) is very similar to the Fowler interaction term [438]

$$\Delta G_I^{\mathrm{E}} = 2Z_1\omega X_I^{\Phi}/X^{0\Phi}, \tag{4.80}$$

where Z_1 is the number of the nearest neighbours in the interface (i.e. lateral co-ordination number) and ω is the pair interaction energy of the I atoms. The combination of (4.32) with (4.79) or (4.80) represents the well-known Fowler segregation isotherm [13, 438].

Analysis of the Fowler isotherm results in an interesting consequence. In case of $\alpha_I^{\Phi} < 0$ (i.e. repulsive *I–I* interaction), the absolute value of the exponential term in (4.32) is reduced, and therefore, the extent of segregation is lowered progressively as X_I^{Φ} grows. On the other hand, if the presence of a segregated atom I enhances the probability of occupation of the nearest neighbour sites by the same kind of the atoms (i.e. positive values of α_I^{Φ} corresponding to attractive *I–I* interaction), the exponential term and the extent of segregation is enhanced with increasing X_I^{Φ}. As α_I^{Φ} becomes more positive, the segregation increases more strongly with decreasing temperature until the rise in segregation becomes eventually discontinuous at the value of $\alpha_I^{\Phi} > 2RT$. This can be documented, for example of selenium and tellurium segregation in iron (Fig. 4.8) [13,307,439] and antimony in iron [416]. It is also well documented in Fig. 4.8, for example of phosphorus segregation in iron [328], that the Langmuir–McLean segregation isotherm (4.65) represents the special case of the Fowler isotherm with $\alpha_I^{\Phi} = 0$. For example, the Fowler type of grain boundary segregation with $\alpha_I^{\Phi} = 2.5RT$ was observed for bismuth in copper [440].

Grain boundary concentration of tellurium at 700°C was found to increase with increasing bulk concentration up to about 100 ppm [441, 442]. This bulk concentration represents probably the limit of solid solubility and beyond this limit, the same amount of tellurium remains dissolved in ferrite solid solution and thus available for segregation while the remaining tellurium precipitates as the second phase. A wide scatter of measured grain boundary concentrations is ascribed to strong anisotropy of grain boundary segregation. Large differences in grain boundary segregation and thus in grain boundary energy result in faceting of grain boundaries, which then exhibit large difference in tellurium content [442].

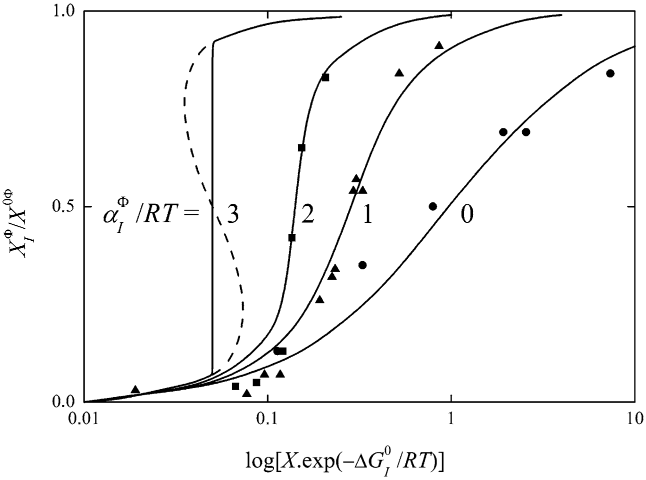

Fig. 4.8 Correlation of experimental data on grain boundary of phosphorus (*circles*) [328], selenium (*triangles*) and tellurium (*squares*) [439] in iron using the Fowler isotherms (according to [308]). The value of the Fowler parameter α_I^Φ/RT (4.71) is marked at individual curves

Fowler model was also used to describe low level of boron grain boundary segregation in ordered polycrystalline Fe–40at.%Al intermetallic alloys [128, 443]. This correlation resulted in the values of ΔG_B^0 ranging from −30 to −34 kJ/mol and α_I^Φ ranging from −110 to 160 kJ/mol. These values suggest strong repulsive interaction between boron atoms. However, we can alternatively fit these experimental data according to the Langmuir–McLean model considering the saturation of the grain boundary. In this case, the ordering of the system and the grain boundary segregation in interstitial positions has also to be taken into account, $X_{\text{tot}}^{0\Phi} = X_{\text{ord}}^{0\Phi} \times X_{\text{int}}^{0\Phi}$. The best fit of the experimental data was obtained using $X_{\text{tot}}^{0\Phi} = 0.058$, which corresponds to the values $X_{\text{ord}}^{0\Phi} = 0.23$ (determined according to (4.70) and (4.71) with $m^\Phi(T = 673\ \text{K}) = 0.77$ using $T_c^\Phi = 1{,}354$ K and $\beta^\Phi \approx 0.5$ [179, 385]) and to $X_{\text{int}}^{0\Phi} = 0.6$ (the fraction of octahedral interstitial positions in bulk bcc lattice), provided the best correlation supposing that about one interstitial positions are occupied per unit cell. The corresponding value of the standard Gibbs energy of segregation was found to be $\Delta G_I^0 = -48$ kJ/mol. As it is apparent from Fig. 4.9, these data fit with the experimental values very well.

Let us compare now the correlation of the segregation data using both the Fowler approach and the site competitive segregation without interaction. It is apparent from Fig. 4.9, that both types of correlation provide us with very similar results [347]. If we compare both types of correlation (i.e. (4.65) with $\Delta G_I^E = 0$ and $X^{0\Phi} \neq 1$ on the one hand, and (4.65) with $X^{0\Phi} = 1$ and ΔG_I^E given by (4.79) on the other hand) and suppose $X_I^\Phi \gg X_I$, we obtain

$$X^{0\Phi} - X_I^\Phi = \left(1 - X_I^\Phi\right) \exp\left(-\Psi X_I^\Phi\right), \tag{4.81}$$

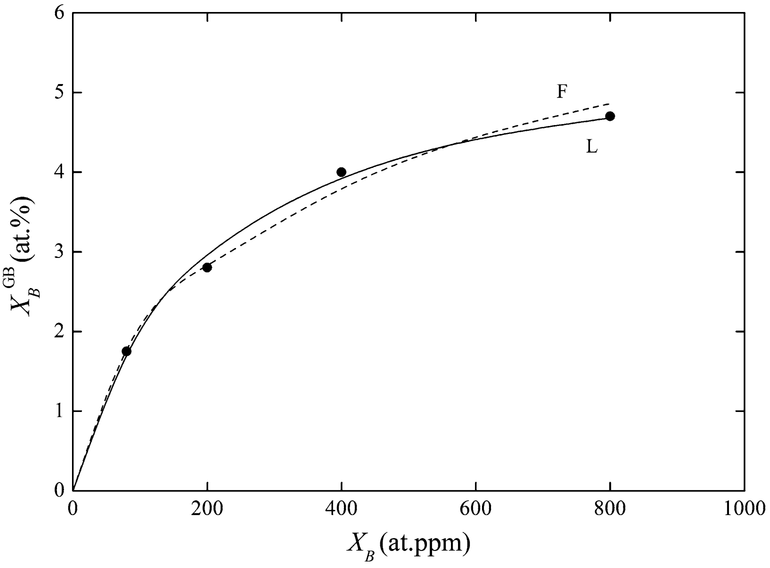

Fig. 4.9 Correlation of the concentration dependence of equilibrium boron segregation at grain boundaries of a polycrystalline Fe–40at. %Al alloy at 673 K (*solid circles*) according to the Langmuir–McLean model with limited number of positions available for segregation $\left(X^{\Phi} = 0.058,\ \Delta G_{\mathrm{B}}^{0} = -48\,\mathrm{kJ/mol}\right)$ (L, *full line*) and the Fowler model ($\alpha_{\mathrm{B}}^{\Phi} = -114\,\mathrm{kJ/mol}$, $\Delta G_{\mathrm{B}}^{0} = -34\,\mathrm{kJ/mol}$) (F, *dashed line*) [347]

where

$$\Psi = -2\alpha_I^{\Phi}/RT. \tag{4.82}$$

Differentiation of (4.81) by X_I^{Φ} results in

$$\exp\left(-\Psi X_I^{\Phi}\right) = \frac{1}{1 + \left(1 - X_I^{\Phi}\right)\Psi} \tag{4.83}$$

and its substitution back in (4.81) provides us with a general expression assuming only $X^{0\Phi} \neq 1$,

$$\frac{1}{\Psi} = \frac{\left(1 - X_I^{\Phi}\right)\left(X^{0\Phi} - X_I^{\Phi}\right)}{1 - X^{0\Phi}}. \tag{4.84}$$

It clearly follows from (4.84) that the Fowler interaction parameter, represented by Ψ, is closely related to the saturation limit: While the negative value of Ψ between segregating atoms corresponds to the solute segregation in more than one monolayer as, for example in the case of bismuth segregation in copper [105] or tin in iron [91], positive values of Ψ are well correlated with a saturation limit for segregation. It is clearly obvious from (4.65) that the value $X^{0\Phi} = 1$ corresponds to ideal Langmuir–McLean behaviour ($\Psi = 0$).

Equation (4.84) suggests that the interaction parameter Ψ should depend on interfacial concentration although it is concentration independent. In fact, however, the value of Ψ changes with the concentration range of the data used for the correlation as can be tested for any experimental or model data. Therefore, the mean value of Ψ for the whole concentration range should be determined as

$$\frac{1}{\Psi^{\mathrm{mean}}} = \frac{\int\limits_0^{X^{0\Phi}} \frac{1}{\Psi} \mathrm{d}X_I^{\Psi}}{\int\limits_0^{X^{0\Phi}} \mathrm{d}X_I^{\Psi}}. \tag{4.85}$$

Substituting (4.84) into (4.85) and integrating it, we obtain

$$\frac{1}{\Psi^{\mathrm{mean}}} = \frac{X^{0\Phi}(3 - X^{0\Phi})}{6(1 - X^{0\Phi})}. \tag{4.86}$$

Supposing low saturation limit for interfacial segregation, that is $X^{0\Phi} \ll 1$ (that is typical for ordered alloys and intermetallics [347]), (4.86) reduces to

$$X^{0\Phi} = \frac{2}{\Psi^{\mathrm{mean}}}. \tag{4.87}$$

Comparing the values of $X^{0\Phi} = 0.06$ for saturated boron segregation in FeAl-based alloys [125,443], and of $2/\Psi^{\mathrm{mean}} = 0.05$ obtained using $\alpha_I^{\Phi} = -114\,\mathrm{kJ/mol}$, exhibits a very good agreement [347].

A close relationship between $X^{0\Phi}$ and α_I^{Φ} (cf. (4.87) and (4.82)) can be well understood because the repulsive interaction between the segregating species prevents the segregation of the same atoms in close vicinity: This fact also can be interpreted as a limitation of the number of the sites accessible for segregation. This close relationship can also be documented by successful correlation of antimony segregation in iron on the basis of both the Fowler model [417] and the Langmuir–McLean model considering the grain boundary saturation [338].

4.3.5 *Other Models for Grain Boundary Segregation*

In this section, there are various approaches listed, which are used to describe the interfacial segregation by phenomenological models based on the chemical potentials. Many of them were developed for surface chemistry, however, due to similarity of the behaviour of free surfaces and internal interfaces they may also be applied to the grain boundaries.

4.3.5.1 Modern Thermodynamic Calculation of Interfacial Properties

Mezey and Giber [444–446] combined (4.34)–(4.36) and obtained an expression

$$\begin{aligned}\kappa_I &= \frac{X_I^{\Phi}/X_I^{\text{bulk}}}{\left[\left(1-X_I^{\Phi}\right)/\left(1-X_I^{\text{bulk}}\right)\right]^{A_I/A_M}} \\ &= \exp\left\{\left(\frac{A_I}{A_M}\right)\left[\frac{\mu_M-\mu_M^{\text{E}}}{RT}\right]-\left[\frac{\mu_I-\mu_I^{\text{E}}}{RT}\right]\right\}, \end{aligned} \tag{4.88}$$

where the parameter κ_I is a modification of the enrichment ratio β_I (cf. (4.19)). Supposing $A_i = A_i^0$ for pure i $(i = I, M)$, $\mu_i^{\text{E}} = \sigma_i^0 A_i^0 + \tilde{\mu}_i^{\text{E}}$, $\mu_i \approx \tilde{\mu}_i^{\text{E}}$, and neglecting lattice distortion effects in the interface for the solvent ($\mu_M(d) \approx 0$), (4.88) can be rewritten as

$$\kappa_I = \exp\left\{\frac{\left(\sigma_M^0-\sigma_I^0\right)A_I^0}{RT}+\frac{\mu_I(d)}{RT}\right\}. \tag{4.89}$$

A detailed analysis showed that the solute I segregates if $\left(\sigma_M^0-\sigma_I^0\right)/\sigma_I^0 \geq 0.05$ or if $\left|\left(\sigma_M^0-\sigma_I^0\right)/\sigma_I^0\right| < 0.05$ and simultaneously $|(r_M-r_I)/r_M| \geq 0.15$, where r_i are the atomic radii of the component elements. A qualitative agreement was found in the case of surface segregation in many systems [446]. This method was also modified to include the effects of the anisotropy of grain boundary energy and the lattice distortion caused by a solute and its release at the interface [447–450]. In this modification, the interfacial concentration X_I^{Φ} of a solute I in a binary system M–I can be expressed as

$$X_I^{\Phi} = X_I C_m C_n C_r, \tag{4.90}$$

where C_m is the configuration term

$$C_m = \left[\left(1-X_I^{\Phi}\right)/(1-X_I)\right]^{q_M}, \tag{4.91}$$

C_n is the dangling bond term

$$C_n = \exp\left[\frac{q_M\alpha_I^0 G_I^a-\alpha_M^0 G_M^a}{RT}\right] = \exp\left[\frac{\left(\sigma_I^0-\sigma_M^0\right)A_M^0}{RT}\right], \tag{4.92}$$

and C_r is the real mixture term

$$C_r = \exp\left[\frac{q_M\Delta\mu_I^{\text{E}}(m)-\Delta\mu_M^{\text{E}}(m)}{RT}\right], \tag{4.93}$$

where

$$\Delta\mu_i^{\text{E}}(m) = -\alpha\mu_i^{\text{E}\Phi}X_i^{\Phi} + (1-2\alpha)\left[\mu_i^{\text{E}}(X_i)-\mu_i^{\text{E}\Phi}\left(X_i^{\Phi}\right)\right]. \tag{4.94}$$

In (4.91)–(4.94), q_M is the molar internal free energy of atomisation, and α_i^0 and α are the parts of G_i^a related to the neighbours missing in the interface, and of μ_i^{E} related to the interactions of the atoms above and below the interface, respectively. The values of individual parameters in the above expressions can be estimated on basis of corresponding values of interfacial energy and molar enthalpy of mixing.

As mentioned above, this method was primarily used for description of surface segregation, especially for determination of the anisotropy of platinum surface segregation on nickel [448–450].

4.3.5.2 Model of Luthra and Briant

Another expression for segregation isotherm was proposed by Luthra and Briant [315],

$$\frac{X_I^\Phi}{X_I^{\mathrm{bulk}}} = \left(\gamma_I^{\mathrm{bulk}}\right)^{1-f_1} \exp\left[\frac{(\sigma_M f_2 - \sigma_I)A_I^0}{RT}\right], \tag{4.95}$$

where γ_I^{bulk} is the activity coefficient of the solute I in bulk, f_1 and f_2 are the parameters reflecting the ratio of the Gibbs energies of the grain boundary and of the bulk, and the ratio of the partial molar surface area of component I in a solution and in pure substance, respectively. σ_M and σ_I are the grain boundary interfacial energies of the matrix element M and of the segregating element I, respectively, and A_I^0 is the standard molar grain boundary area of the component I [315]. Similarly to the Guttmann model, this approach tries to correlate the non-ideal behaviour of the segregating system by considering the activity coefficients of the components. However, the values of some of the above parameters are not known and therefore, are used as fitting parameters. In fact, it is an analogous approach to that used in the Guttmann model [313], where the non-ideal behaviour of the system is correlated by the regular (quasichemical) approximation. Guttmann model allows simple prediction of both segregation enthalpy and entropy as the fundamental characteristics of interfacial segregation, together with the ternary interaction coefficients that are clearly defined [375]. In fact, the interaction parameters in Guttmann approach on one hand and γ_i and f_i in Luthra and Briant model are not known and represent exclusively the correlation of the non-measurable parameter ΔG_I^{E}, that is from this point of view, both models are very similar. The main drawback of the approach of Luthra and Briant [315] is the physically incorrect basic assumption $\mu_I^{\mathrm{bulk}} = \mu_I^\Phi$ ([310], see above), in which the presence of the matrix element in segregating system is completely ignored. This assumption should have a strict consequence that the grain boundary enrichment ratio β^Φ (4.19) is independent of the nature of the matrix element. However, the measured values of β^Φ for a solute in different matrices exhibit large differences, for example in case of phosphorus, $\beta_{\mathrm{P}}^\Phi \approx 3 \times 10^4$ in tungsten while $\beta_{\mathrm{P}}^\Phi \approx 200$ in bcc iron [168] and in case of boron, $\beta_{\mathrm{B}}^\Phi \approx 5 \times 10^3$ in bcc iron [138] while $\beta_{\mathrm{B}}^\Phi \approx 10$ in $\mathrm{Ni_3Al}$ [425]. Proper derivation based on realistic starting conditions should result in more realistic formulae, which can be used to describe grain boundary segregation in multicomponent alloys. Equation (4.95) could be applied, however, for dilute systems with negligible bulk as well as interfacial concentration of the solute I.

4.3.6 Models for Different Segregation Sites

As it was mentioned in Chap. 2, different grain boundaries possess different structures as characterised by the structural units of individual interfaces. Each structural unit consists of several atoms with different binding energies [275]. In consequence, the Gibbs energy of segregation will also differ for various grain boundary positions of the solute atoms. Similarly, different values of ΔG_I^0 will be found for different grain boundaries. In polycrystalline materials, a spectrum of the segregation Gibbs energies thus exists determining the equilibrium composition of individual grain boundaries. However, only a single value of ΔG_I^0 is involved in the segregation isotherms mentioned above. The only physically meaningful value of ΔG_I^0 is that corresponding to the solute segregation at a particular position of a given grain boundary [451]. Such localised segregation, however, is hardly experimentally measurable at present state-of-art of the detection methods (cf. Chap. 3) and therefore, there is a lack of information about the local environment of the segregated atom [44]. The above given segregation isotherms can thus correctly be applied only to the determination of characteristic thermodynamic parameters of segregation of an element at a chosen grain boundary in bicrystal from the temperature dependence of its chemical composition providing low-grain boundary concentrations. Only in this case, one may expect that the solute atoms segregate at identical grain boundary sites (causing the highest reduction of the Gibbs energy of the system) [20]. An application of the above-outlined segregation isotherms for description of the grain boundary segregation in polycrystals only provides the values of the characteristic parameters averaged over the large spectrum of grain boundaries and grain boundary sites with little physical meaning [342]. On the other hand, there were developed several models for describing the segregation at different grain boundary sites.

4.3.6.1 BET Isotherm

In case of free surfaces, there is a well-known BET theory [452] describing multilayer surface gas adsorption accounting for different energetic states of atoms in individual layers. Let us assume that the surface is filled by solute atoms as shown in Fig. 4.10. There are n_1 sites on the surface occupied by one atom of solute, n_2 sites occupied by two atoms, etc. It is assumed that the Gibbs energy of adsorption in the first layer, ΔG_I^1, has a particular value while its value in higher layers, ΔG_I^i, is equal to the Gibbs energy of condensation [453]. In case of interfacial segregation, we can consider it as two (or more) different values of the Gibbs energy of segregation. It is also supposed that the adsorption/desorption processes occur exclusively

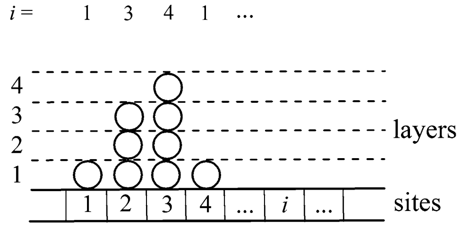

Fig. 4.10 Schematic depiction of formation of multilayer segregation in BET model

between the interface and the bulk, and the atoms are not allowed to move from one layer to another. In equilibrium, the rates of adsorption and desorption for each layer must be identical. Based on these assumptions, the BET isotherm is formulated as

$$\theta^{\Phi} = \frac{X_I \exp\left[-\left(\Delta G_I^i - \Delta G_I^1\right)/RT\right]}{\left(1 - X_I\right)\left\{1 - X_I + X_I \exp\left[-\left(\Delta G_I^i - \Delta G_I^1\right)/RT\right]\right\}}. \tag{4.96}$$

It is apparent that for low bulk concentrations X_I, the Langmuir-McLean isotherm (4.61) is obtained [452]. Principally, (4.96) can be extended to involve several different values of ΔG_I^i and be thus able to describe the segregation to different interfacial positions.

BET approach was applied to describe the grain boundary segregation of tin in bcc iron [306, 307], and to interpret sulphur, phosphorus and antimony segregation in iron and nickel [454]. Multilayer segregation was also detected in other systems such as tellurium and selenium in bcc iron, phosphorus in tungsten and bismuth in copper (cf. [92]).

4.3.6.2 Individual Site Models

Assuming a grain boundary containing N distinct sites of different values of the standard Gibbs energy of segregation, $\Delta G_{I,k}{}^0 (k = 1, \ldots, N)$, White et al. extended McLean treatment for a binary *M–I* system [455, 456]. In their model, the interfacial concentration of the solute I, $X_{I,k}^{\Phi}$, at position k is given by

$$X_{I,k}^{\Phi} = \frac{X_I \exp\left(-\Delta G_{I,k}^0/RT\right)}{1 + X_I\left[\exp\left(-\Delta G_{I,k}^0/RT\right) - 1\right]}. \tag{4.97}$$

The total experimentally observable atom fraction of the solute at the interface, X_I^{Φ}, would then be a weighted average summed over all interfacial sites with the fraction F_k of the total sites at the interface having the same value of the standard Gibbs energy of segregation,

$$X_I^\Phi = \sum_k^N F_k X_{I,k}^\Phi. \tag{4.98}$$

Nowicki and Biscondi [457, 458] modified this approach by normalisation of the parameters per unit area,

$$F_k = \frac{Q_k}{P'}, \tag{4.99}$$

where P' is the mean surface atomic density of the solvent in the volume and Q_k is the number of sites of type k per unit area. According to this model, it is possible to compare the results of the calculated values of the Gibbs energy of segregation with the measurements of the grain boundary concentration at different temperatures and different grain boundaries [458]. In this way, similar values $\Delta H_\mathrm{O}^0 \approx 232\,\mathrm{kJ/mol}$ were determined for oxygen segregation at different sites of the 32°[100], {027} symmetrical tilt grain boundary in molybdenum [457] although such value seems to be unexpectedly high. Similar approach was also used by Rittner [219], Udler and Seidman [332] and Kirchheim [459, 460]. Equations (4.97)–(4.99) can be applied for dilute binary systems. In more concentrated systems, it is necessary to consider the solute–solute interaction and to approximate them, for example according to a simple mean field or quasichemical approach. The Fowler interaction term will then additionally appear in (4.97).

On the other hand, Suzuki [461] supposes that the average amount of the segregated species, X_av^Φ, must reflect the structural effect of the distribution of the Gibbs energy of segregation,

$$X_\mathrm{av}^\Phi = \int_0^\infty X_I^\Phi(\Delta G_I) f(\Delta G_I) \mathrm{d}\Delta G_I, \tag{4.100}$$

where $f(\Delta G_I)$ is the distribution function of the Gibbs energy of segregation and $X_I^\Phi(\Delta G_I)$ is the concentration of solute I at a grain boundary with the Gibbs energy of segregation ΔG_I. In the simplest case, the Gaussian distribution can be taken to represent the distribution function $f(\Delta G_I)$. A comparison of the model calculations of phosphorus segregation in α-iron with experimental data of Erhart and Grabke [328] documented the difference of the thermodynamic parameters characterised mainly by an underestimation of the segregation enthalpy in the experiments being performed on polycrystals.

4.4 Models for Thermodynamic Functions of Interfacial Segregation

The phenomenological theories presented above can provide us with the values of thermodynamic and/or interaction parameters of the grain boundary segregation by fitting the experimental data. Knowledge of the values of ΔH_I and ΔS_I is, however, essential for an estimate of the segregation behaviour of a chosen system. Therefore, considerable effort has been spent to develop methods, which could enable assessing the values of these functions on basis of the state of atomic bonding and structural factors at individual interfaces. Since the structure and bonding are simpler for free surfaces than for grain boundaries, the majority of the theories to predict thermodynamic parameters of solute segregation were originally developed for free surfaces. Because of similarity of the nature of free surfaces and internal interfaces and analogous description of their segregation behaviour, the theoretical models developed for free surfaces can be modified to describe the grain boundary segregation. However, their application requires further assumptions to be made, mainly with respect to structural details of the grain boundaries. Although these models have been used only rarely to evaluate the thermodynamic parameters of the grain boundary segregation, a brief description of some models is given here.

4.4.1 Model of Wynblatt and Ku

Wynblatt and Ku [324,325] modified the so-called bond-breaking model of Williams and Nanson [462] based on the enthalpies of formation and mixing to calculate the enthalpy and entropy of interfacial segregation. The model considers the contribution of two different terms, the bond alteration at the interface or "chemical" contribution, $\Delta H_I^{\mathrm{chem}}$ [463], and the elastic strain energy relief, ΔH_I^{el} [19, 464], which may be modified by the electronic density relaxation [465]. The total enthalpy of interfacial segregation is then

$$\Delta H_I = -\Delta H_I^{\mathrm{el}} + \Delta H_I^{\mathrm{chem}}. \tag{4.101}$$

The elastic enthalpy term arises from the mismatch between the atoms of solute I and solvent M and is generally expressed as [19, 138, 324, 466]

$$\Delta H_I^{\mathrm{el}} = \frac{24\pi B\mu r_I r_M (r_I - r_M)^2}{3Br_I + 4\mu r_M}, \tag{4.102}$$

where B is the bulk modulus of solute I, μ is the shear modulus of solvent M and r_I and r_M are the effective radii of the solute and solvent, respectively. The term $\Delta H_I^{\mathrm{chem}}$ is defined by the energy change if an atom M is replaced by an atom I at the interface. In the regular solution approximation,

$$\Delta H_I^{\mathrm{chem}} = (\sigma_I - \sigma_M)A^{\Phi} - \frac{2\Delta_m H}{ZX_I X_M}\left[Z_{\mathrm{L}}\left(X_I^{\Phi} - X_M\right) + Z_{\mathrm{P}}\left(X_I - \frac{1}{2}\right)\right]. \tag{4.103}$$

Here σ_i are the interfacial energies of pure components ($i = I, M$), A^{Φ} is the interface area per atom, $\Delta_m H$ is the enthalpy of mixing of the $M{-}I$ alloy, Z is the co-ordination number of mixing in bulk, and Z_{L} and Z_{P} are the lateral and the perpendicular co-ordination numbers, respectively, of an atom in the interface layer.

This combined model reflects three principal contributions to the interfacial segregation in metallic systems (a) the *chemical driving force* represented by the difference of the interfacial energy of pure components M and I (cf. (4.103)); (b) *interatomic driving force* depending on the regular solution constant (4.103) which vanishes in the case of ideal solution ($\Delta_m H = 0$) and (c) *elastic driving force* represented by the strain energy contribution reflecting the degree of the misfit of the solute in a solution (4.102) that also vanishes in ideal system [303]. ΔH_I thus involves both the ideal contribution of the grain boundary energy to the segregation enthalpy and the excess term and thus differs from the standard enthalpy of grain boundary segregation. It follows from (4.101)–(4.103) that the standard enthalpy of segregation is $\Delta H_I^0 = (\sigma_I - \sigma_M)A^{\Phi}$ [113,303] although the enthalpy contribution to interfacial Gibbs energies σ_i should only be taken into account,

$$\Delta H_I^0 = \left(h_I^{\Phi} - h_M^{\Phi}\right) A^{\Phi}. \tag{4.104}$$

Correspondingly, the entropy of segregation, ΔS_I, is also composed of one elastic and two chemical contributions [325],

$$\begin{aligned}\Delta S_I = (s_I - s_M)A^{\Phi} - \frac{2\Delta_m S}{Z X_I X_M}\left[Z_{\mathrm{L}}\left(X_I^{\Phi} - X_M\right) + Z_{\mathrm{P}}\left(X_I - \frac{1}{2}\right)\right] \\ + \frac{\mathrm{d}}{\mathrm{d}T}\left[\frac{24\pi B\mu r_I r_M (r_I - r_M)^2}{3Br_I + 4\mu r_M}\right],\end{aligned} \tag{4.105}$$

where $\Delta_m S =$ is the excess entropy of mixing of the alloy $M{-}I$, and s_I and s_M are the specific interfacial entropies of the pure components. These three terms can either be of the same sign to reinforce each other or have different signs to partially cancel out. Generally, $|\Delta S_I|$ will be large when $|\Delta H_I|$ possesses large value [303]. This is compatible with the compensation effect (see Chap. 5). Similarly to ΔH_I^0, the standard entropy of grain boundary segregation should be given as

$$\Delta S_I^0 = \left(s_I^{\Phi} - s_M^{\Phi}\right) A^{\Phi}. \tag{4.106}$$

In metals, the grain boundary energy is relatively small and the difference $\sigma_I - \sigma_M$ is less important than for free surfaces [467]. Therefore, the term $\Delta_m H$ has comparatively larger influence. If $\Delta_m H < 0$, the segregation enthalpy is lowered, the system tends to ordering and oscillations of the concentration in deeper layers are predicted [324,467]. If $\Delta_m H > 0$, the binary system has the properties representative of a miscibility gap [303] and the segregation is enhanced, which can lead to clustering, that is to multilayer segregation [467]. Later, the theory of Ku and Wynblatt was extended to ternary alloys $M{-}I-J$ by extending the right side of (4.103) by the term [468]

$$\frac{1}{Z}\left[\frac{\Delta_m H_{IJ}}{X_I X_J} - \frac{\Delta_m H_{IM}}{X_I(1-X_I-X_J)} - \frac{\Delta_m H_{JM}}{X_J(1-X_I-X_J)}\right] \times\left[Z_{\mathrm{L}}\left(X_I^{\Phi}-X_I\right)+Z_{\mathrm{P}}X_I\right]. \tag{4.107}$$

In contrast to metallic materials, the following driving forces controlling grain boundary segregation in ceramic materials can be distinguished (a) elastic; (b) electrostatic and (c) dipole interactions [468,469]. The elastic term arises from interactions between solutes and the ceramic interface due to the space charge and can be expressed as

$$\Delta_{\mathrm{el}} H_I = -\frac{6B\pi r_M (r_I - r_M)^2}{1+3B/4\mu}. \tag{4.108}$$

The electrostatic term arises from interactions between solutes and the ceramic interface due to the space charge and can be written as

$$\Delta_{\mathrm{e}} H_I = -\frac{1}{2}\rho u^{\Phi}. \tag{4.109}$$

where ρ is the charge density and u^{Φ} is the potential distribution in the interface. The third contribution stems from the tendency of the charged solutes to combine with the defects of the opposite charge in a ceramics, and to form electrically neutral complex with a dipole moment. It is given by

$$\Delta_{\mathrm{d}} H_I = -\frac{1}{2}Ep, \tag{4.110}$$

where E is the electric field and p is the dipole moment [469].

4.4.2 Model of Seah

According to Seah [13, 371], ΔS_I^0 generally consists of three contributions that are associated with changes of vibrational $\left(\Delta S_I^{\mathrm{vib}}\right)$, anharmonic $\left(\Delta S_I^{\mathrm{an}}\right)$ and site multiplicity $\left(\Delta S_I^{\mathrm{mult}}\right)$ entropies. In general, ΔS_I^{an} and $\Delta S_I^{\mathrm{mult}}$ can be neglected in comparison to $\Delta S_I^{\mathrm{vib}}$, which is expressed as the change of the Debye temperature for a solute in the matrix and at the interface [13, 371, 470]

$$\Delta S_I^{\mathrm{vib}} = 3R\left[1+\ln\left(\frac{kT}{h\nu_I}\right)\right], \tag{4.111}$$

where $kT \gg h\nu_I$, ν_I is the Einstein frequency and $h\nu_I$ may be rewritten as $k\theta_{\mathrm{E},J}$ or $0.775k\theta_{\mathrm{D},J}$ where $\theta_{\mathrm{E},J}$ and $\theta_{\mathrm{D},J}$ are Einstein and Debye temperatures, respectively, so that

$$\Delta S_I^{\mathrm{vib}} = 3R\ln\left(\frac{\theta_{\mathrm{D},J}}{\theta_{\mathrm{D},J}^*}\right), \tag{4.112}$$

where $\theta^{*}_{\mathrm{D},J}$ is the Debye temperature for the solute atom at the distorted site of the interface. Often, it is supposed that the entropy is controlled by the vibrational term and that $|\Delta S_I^{\mathrm{vib}}| < 3.3RT$ [13, 299, 300, 371]. However, much higher values of segregation entropy were reported in literature, for example $\Delta S^0_{\mathrm{P}} \approx 5.4R$ was found for the {013} grain boundary in bcc iron [111] and $\Delta S^0_{\mathrm{C}} \approx 5.2R$ for carbon segregation in polycrystalline bcc iron [355]. High values of segregation entropy were also determined theoretically ($\Delta S^0_{\mathrm{Sn}} \approx 5.4R$ for $T \leq 1{,}184$ K and ($\Delta S^0_{\mathrm{Sn}} \approx 6.4R$ for $T \geq 1{,}184$ K) [371]. The origin of the high values of segregation entropy conveys with the compensation effect discussed in Chap. 5.

4.4.3 Model of Miedema

Solute segregation in alloys of transition metals can be determined considering the effects of (a) the heat of solution, (b) the differences in interfacial energy of pure metals and (c) the elastic size mismatch energy [465]. Miedema established the basic expression for interfacial segregation in binary $M-I$ alloy,

$$\frac{X_I^{\Phi}}{X_I} = \exp\left\{\left[f\Delta_{\mathrm{sol}}H_{MI} - g\left(H_I^{\Phi} - H_M^{\Phi}\right)V_I^{2/3}\right]/RT\right\}, \tag{4.113}$$

where $\Delta_{\mathrm{sol}}H_{MI}$ is the enthalpy of solution of I in M, $H^{\Phi}_{M,I}$ is the interfacial enthalpy of M and I and f and g are constants. The interfacial enthalpies are obtained from an empirical theory considering two basic parameters: the electrochemical parameter, u^* and the charge parameter, $\rho^{1/3}$. Δu^* serves as the measure of the charge transfer between metals I and M, and $\Delta\rho^{1/3}$ reflects the difference in interfacial tension between the elemental metals. The difference of the interfacial energies of the two pure metals is generally controlling the segregation behaviour [465]. This easy method offers a very realistic view on surface segregation in many systems [471].

4.4.4 Model of Kumar

Kumar [472] used the bond-breaking model to extend a quasichemical formulation for chemical composition at the surfaces of non-regular solid solutions. Considering only the nearest-neighbour interactions, different behaviour of individual layers parallel to the interface and the equal relaxations for all bonds, the enthalpy of segregation, ΔH_I, in the interface layer in a I_xM_y binary alloy can be expressed as

$$\Delta H_I = \frac{\varepsilon_{II} - \varepsilon_{MM}}{2}\left[Z - (Z_{\mathrm{L}} + Z_{\mathrm{P}})(1+\alpha)\right], \tag{4.114}$$

where ε_{ii} are the bond enthalpies for the ii-type nearest neighbour pair. Z, Z_L and Z_P are the total, interlayer and intralayer numbers of the nearest neighbours of an atom in the interfacial layer, respectively, and α is the relaxation parameter. The segregation entropy can be expressed in a similar way. A good agreement between the results obtained according to this model and experimental data was found for surface segregation in silver–gold and copper–nickel systems.

4.4.5 Model of Mukherjee and Morán-López

According to this model based on a simple tight-binding theory of the surface segregation in alloys of transition metals [473, 474], the equilibrium interface composition of an $I_X M_Y$ alloy can be determined by minimising the total free energy

$$F(X_0, X_1, \ldots, X_N) = \sum_{\lambda} [E_\lambda + kT(X_\lambda \ln X_\lambda + Y_\lambda \ln Y_\lambda)] - \mu N \sum_{\lambda} X_\lambda \tag{4.115}$$

with

$$E = -\frac{1}{2} W_n (1-n) + n\varepsilon_0, \tag{4.116}$$

$$W_{MI}^2 = 12\left[XY(\varepsilon_I - \varepsilon_M)^2 + (XW_I + YW_M)^2/Z\right] \tag{4.117}$$

and

$$\begin{aligned}\left(W_{MI}^{\Phi}\right)^2 = 12[&X_0 Y_0 \left(\varepsilon_I^{\Phi} - \varepsilon_M^{\Phi}\right)^2 + Z_\mathrm{L}(X_0 W_I + Y_0 W_M)^2/Z^2 \\ &+ Z_\mathrm{P}(X_0 W_I + Y_0 W_M)(XW_I + YW_M)/Z^2].\end{aligned} \tag{4.118}$$

In (4.115)–(4.118), X and Y denote the bulk composition of the alloy $I_X M_Y$ and Y_λ are the compositions of individual surface ($\lambda = 0$) and subsurface layers $(1, \ldots)$, W is the bandwidth centred at the energy ε_0, and n is the fractional occupation number. W_{MI} and W_{MI}^{Φ} are the effective bandwidths in the bulk and at the surface, respectively, ε_i^{Φ} and ε_i are the centres of the surface and the bulk d-bands of the pure metals i ($i = I, M$), respectively. Z, Z_L and Z_P are the bulk, intralayer and interlayer coordination numbers, respectively. Mukherjee and Morán-López used a rectangular shape of the d-band density of states with the bandwidth, band centre and band filling as only input parameters and predicted the surface segregation for any binary alloy of transition metals. In contrast to the model of Miedema [465,470], the equilibrium surface concentration can be calculated for any bulk composition as a function of temperature [473].

4.4.6 BFS Model

Bozzolo, Ferrante and Smith developed a technique for calculating the alloy properties such as the heat of formation [475], the surface energy of binary alloys [476] and the heat of segregation of substitution impurities [477,478]. Based on their BFS model, the energy of segregation, ΔE_I^{seg}, is defined as the difference between the heat of formation of a semi-infinite crystal M with an impurity I located at a lattice site on a plane parallel to the surface and the heat of formation of the same structure but with the atom I located in a lattice site in the bulk. In this way, ΔE_I^{seg} can be expressed (analogously to the model of Wynblatt and Ku) as a sum of two contributions, the strain term, $\Delta E_I^{\text{strain}}$, and the chemical term, ΔE_I^{chem},

$$\Delta E_I^{\text{seg}} = \Delta E_I^{\text{chem}} + \Delta E_I^{\text{strain}}, \tag{4.119}$$

where

$$\Delta E_I^{\text{strain}} = e_I^{\text{strain},\Phi} - e_I^{\text{strain,bulk}} - e_M^{\text{strain},\Phi} \tag{4.120}$$

and

$$\begin{aligned}\Delta E_I^{\text{chem}} = {} & \sum_q g_{Mq}\left[f_q^{\Phi} e_{Mq}^{\prime\text{chem}} + g_q^{\Phi} e_{Mq}^{\prime\prime\text{chem}}\right] - N_1 e_{Mb}^{\prime\text{chem}} \\ & - N_2 e_{Mb}^{\prime\prime\text{chem}} + g_{I\Phi} e_I^{\text{chem},\Phi} - g_{Ib} e_I^{\text{chem},b}\end{aligned} \tag{4.121}$$

In (4.120) and (4.121), e_i^{strain} and e_i^{chem} are the strain and chemical energies, respectively, of atoms i $(i = I, M)$ at the interface Φ and in the bulk. G_i are the coupling terms of i at the interface and in the bulk b and $e_{Mq}^{\prime\text{chem}}$ and $e_{Mq}^{\prime\prime\text{chem}}$ are the chemical energies between atoms for the nearest and the next-nearest neighbours, respectively, at the qth layer. N_1 and N_2 are the total numbers of the nearest and the next-nearest neighbours, respectively, and f_q^{Φ} and g_q^{Φ} are the numbers of the nearest and the next-nearest neighbours, respectively, in layer q in respect to the atom located in layer Φ. Equations (4.119)–(4.121) were derived for the unrelaxed thermodynamic state. Monte Carlo calculations at zero temperature enable selected atoms to undergo relaxation and provide relaxed configurations and, thus, the segregation energies. Individual parameters of the BFS theory are determined from pure elemental data and from only two-alloy properties [478].

BFS model has successfully been tested for surface segregation [477] but can be extended to the grain boundaries after appropriate modification. The main advantage of this model is that it allows the derivation of simple approximate expressions describing the trends in segregation as well as the elucidation of driving mechanisms for these phenomena.

4.4.7 SMA–TBIM Approach

To study interfacial segregation, a tight-binding Ising model (TBIM) used for studies of the surface segregation [479, 480] was extended to the grain boundary segregation assuming that the energetic parameters of the Ising model are determined by atomistic simulations utilising atomic potentials derived from the second-moment approximation (SMA) of the tight-binding scheme [481, 482]. Using the tight-binding Hamiltonian and generalised perturbation method, an effective Ising Hamiltonian can be obtained. By means of this Hamiltonian, the part of the energy that depends on chemical configuration can be calculated. Supposing the simplest case, the index of the possible sublattices is omitted. Then, the concentration X_I^p of solute I in pth plane parallel to the grain boundary plane can be determined according to [481,482] as

$$\frac{X_I^p}{1-X_I^p} = \frac{X}{1-X}\exp\left(-\frac{\Delta G_{I,p}}{RT}\right). \tag{4.122}$$

In (4.122), $\Delta G_{I,p}$ is the Gibbs energy of segregation of I at pth plane. The enthalpy part, $\Delta H_{I,p}$, consists of two contributions – the standard and the excess enthalpies,

$$\Delta H_{I,p} = \Delta H_{I,p}^0 + \Delta H_{I,p}^{\mathrm{E}}, \tag{4.123}$$

where the concentration-dependent excess contribution takes into account for the interaction between the segregating atoms,

$$\Delta H_{I,p}^{\mathrm{E}} = 2\sum_R \left(\sum_{p'=-q}^{p'=+q} Z_R^{p,p+p'} V_R^{p,p+p'} X_{I,p+p'} - Z_R V_R X_I \right). \tag{4.124}$$

In (4.124), $V_R = \left(V_R^{AA} + V_R^{BB} - 2V_R^{AB}\right)/2$ is the effective pair interaction energy between Rth neighbours, Z_R is the bulk co-ordination number for the Rth shell of neighbours, $Z_R^{p+p'}$ is the number of Rth neighbours between planes p and p'. The index q defines the number of planes that have to be considered ($2q + 1$ in bulk) consistently with the spatial extension of V_R. The effective pair interactions can vary at the interface. This explains the occurrence of the exponent in $V_R^{p,p+p'}$ in the term depending on $X_{I,p+p'}$ [482]. The term $\Delta H_{I,p}^0$ consists of three contributions [479,481],

$$\Delta H_{I,p}^0 = \Delta H_{I,p}^{\mathrm{size}} + \Delta H_{I,p}^{\mathrm{site}} + \Delta H_{I,p}^{\mathrm{EPI}}, \tag{4.125}$$

that is (a) of the size mismatch between solute I and matrix M, (b) of the difference of sites on the pth plane between the pure constituents and (c) of the effective pair interaction, respectively [482]. The latter term is related to V_R

$$\Delta H_{I,p}^{\mathrm{EPI}} = \sum_{R} V_R \left(Z_R - \sum_{p'=-q}^{p'=+q} Z_R^{p,p+p'} \right). \tag{4.126}$$

The most important result of the SMA-TBIM model is the determination of the energetic parameters of (4.123)–(4.126) on basis of realistic simulations [481, 483]. N-body atomic potentials may be derived from the SMA of the tight-binding scheme [482, 484]. Minimisation of the enthalpy with respect to atomic positions done by quenched molecular dynamics algorithm results in the value of $\Delta H_{I,p}^{\mathrm{site}}$. To calculate $\Delta H_{I,p}^{\mathrm{size}}$, the atomic potentials are the same for the *I–I, M–M* and *I–M* interactions except that fixing the lattice parameter for each metal. Thus, the size effect is separated from the site and effective pair interaction effects. V_R can be obtained by considering the difference of the enthalpy of a relaxed system, ΔH_R, containing two isolated solute atoms (initial state) and of two solute atoms in Rth neighbour positions (final state), $V_R = \Delta H_R/2$ [483].

The vibrational part of the segregation entropy which is involved in $\Delta G_{I,p}$ and $\Delta S_{I,p}$ can be estimated by a recursion method [485] using the relaxed values of the atomic positions and the force constants obtained on the basis of SMA potential [482].