Complexions in a modified Langmuir-McLean model of grain boundary segregation

S.R. Wilson

Abstract

The Langmuir-McLean isotherm is often interpreted as providing an approximation to the most probable grain boundary segregation as a function of the bulk mole solute fraction $x_B$, even though $x_B$ is not an independant parameter in the free energy minimization on which it is based. In this paper it is shown that the most probable segregation for a specified $x_B$ differs from the standard Langmuir-McLean relation. Numerical solution of the derived equation suggests that two potentially stable interface compositions are associated with most bulk compositions. One solution represents a state with an excess of solute along the boundary relative to the bulk, while the other represents a deficit. The vacancy content ratio between the interface and the bulk plays a large role in determining the shape of the derived isotherm.

Keywords: segregation, complexion, grain boundary, solute

1 Introduction

Segregation is the process of grouping impurities and structural defects together in a material system [1,2]. Any free energy reduction associated with segregation can be leveraged to stabilize a desired defect structure, allowing materials engineers to “bake in” what would otherwise be transitory material properties that depend on the dominant defect population. [3,4]

Segregation has therefore been the subject of much research in metallurgy and materials science from its initial roots [5] to the present day [6,7,8,9]. The simplest model of equilibrium segregation along a grain boundary is given by the Langmuir-McLean isotherm [10,11]

$$\frac{\Gamma_B}{\Gamma_0 - \Gamma_B} = \frac{x_B}{x_A} e^{-\delta G/k_B T}$$

(1)

where $\delta G$ is the segregation free energy per solute atom, $k_B$ is Boltzmann’s constant, $T$ is the ambient temperature, $\Gamma_B$ is the number density of solute atoms segregated to the boundary with maximal value $\Gamma_0$, and $x_B$ and $x_A$ are the mole fractions of components A and B in the bulk.

The Langmuir-McLean isotherm serves as a common touchpoint for a number of segregation models proposed over the years on the basis of more complicated assumptions. A few of the more prominent models include the Fowler-Guggenheim isotherm [12], which considers the influence of solute-solute interactions in the interface, and the Seah-Hondros isotherm [13], derived on the basis of solid-state theoretic methods.

Despite these efforts, there remains a significant discrepancy between the observed and predicted segregation to interfaces in many real materials [14]. In this paper I present a simple modification to the Langmuir-McLean model that yields very different predictions.

2 Model derivation

Equation (1) results from analyzing a two-state model of a grain boundary in which impurity atoms of component B are either segregated to the interface or are free to roam in a bulk matrix consisting of atoms of component A. The same two-state system will be considered in this work. A brief outline of the steps involved in the derivation of equation (1) will be presented before indicating the changes proposed.
in this paper.

Distribute $n_A = n_{A0} + n_{A1}$ atoms of component A and $n_B = n_{B0} + n_{B1}$ atoms of component B among $N_1$ indistinguishable bulk sites and $N_0$ indistinguishable interface sites, such that $n_{B0}$ and $n_{A0}$ are situated on the interface while the rest remain in the bulk. The quantity of primary interest is $n_{B0}$, because this represents the number of atoms of component B segregated to the interface. Subscript 1 will indicate bulk quantities; subscript 0 will indicate interface quantities.

The most probable number of segregated solute atoms, $n_{B0}$ minimizes the Helmholtz free energy $F = U - TS$ in the NVT ensemble. To find this minimum, we can express both the internal energy $U$ and the entropy $S$ as functions of $n_{B0}$ and evaluate $\partial F/\partial n_{B0} = 0$. An expression for the entropy $S = k_B \ln \Omega$ may be determined by counting the total number $\Omega$ of indistinguishable configurations of the system that correspond to a specified system configuration $\{n_{A0}, n_{A1}, n_{B0}, n_{B1}\}$. Basic combinatorics yields

$$\Omega = \frac{N_1!}{n_{B1}!n_{A1}!n_{V1}!} \cdot \frac{N_0!}{n_{B0}!n_{V0}!},$$

where $n_{V1} = N_1 - n_{A1} - n_{B1}$ and $n_{V0} = N_0 - n_{A0} - n_{B0}$ are the number of vacant sites in the bulk and in the interface. Using this expression, it can be shown that the general solution to $\partial F/\partial n_{B0} = 0$ in the Stirling approximation satisfies

$$n_{B0}^{n_{A0}} n_{V0}^{n_{V0}} = n_{B1}^{-n_{B1}'} n_{A1}^{-n_{A1}'} n_{V1}^{-n_{V1}'} e^{-\delta G/k_B T},$$

where $\delta G = \partial U/\partial n_{B0}$ is the segregation free energy and primes indicate differentiation with respect to $n_{B0}$. In order to evaluate the primed exponents that appear in equation (3), it is necessary to specify how each variable depends on $n_{B0}$. The Langmuir-McLean isotherm therefore represents the most probable segregation for a given bulk atom density $n_1$. Let us instead seek the most probable segregation for a specified bulk impurity composition $x_{B1}$. To do so, consider replacing constraint (3) with the equation $n_{B1}/n_{A1} = r$, where $r$ is a fixed positive number. Fixing $r$ also fixes $x_{B1}$ because $x_{B1} = r/(1 + r)$. It can be shown that in this case we have $n_{A0}' = 1/r, n_{A1}' = -1/r, n_{B1}' = -1, n_{V0}' = -(1 + r)/r, and n_{V1}' = (1 + r)/r$, leading to

$$n_{B0} n_{A0}^{1/r} n_{V0}^{-(1+r)/r} = n_{B1} n_{A1}^{1/r} n_{V1}^{-(1+r)/r} e^{-\delta G/k_B T},$$

where all quantities on the right-hand side are considered to be independent of $n_{B0}$. The first two constraints follow from conservation of atom number by component; the second two from conservation of site number; and the last constraint neglects vacancies in the interface. From these constraints, we can see that $n_{A0}' = -1, n_{A1}' = 1, n_{B1}' = -1, n_{V0}' = 0$, and $n_{V1}' = 0$. Substituting these values into equation (3) and rearranging leads to equation (1), after identifying $x_A = n_{A1}/(n_{A1} + n_{B1}), x_B = n_{B1}/(n_{A1} + n_{B1}), \Gamma_B/\Gamma_0 = n_{B0}/N_0 = x_{B0}$, and $x_{A0} = 1 - x_{B0}$.

A similar result may be obtained by replacing the final constraint (8) with the equation $n_{A1} + n_{B1} = n_1$, which permits the interface and the bulk to exchange an atom of component A for an atom of component B while allowing no change in the total number $n_1$ of atoms in the bulk. This relation leads to the same set of exponents as in the previous case, but the interface vacancy content is no longer necessarily zero. As a consequence we must write $x_{B0} = (1 + x_{V0}) \Gamma_B/\Gamma_0$ and equation (1) instead reads

$$\frac{\Gamma_B}{\Gamma_V - \Gamma_B} = \frac{x_{B1}}{x_{A1}} e^{-\delta G/k_B T},$$

with $\Gamma_V \equiv \Gamma_0/(1 + x_{V0})$. This constraint accounts for interface vacancies by normalizing the maximum segregation to match a given interface vacancy content. In either case, the nature of the final constraint indicates that this relation best models segregation in a system that does not allow variable vacancy content, whether in the interface or in the bulk.

The Langmuir-McLean isotherm therefore represents the most probable segregation for a given bulk atom density $n_{A1}$. Let us instead seek the most probable segregation for a specified bulk impurity composition $x_{B1}$. To do so, consider replacing constraint (3) with the equation $n_{B1}/n_{A1} = r$, where $r$ is a fixed positive number. Fixing $r$ also fixes $x_{B1}$ because $x_{B1} = r/(1 + r)$. It can be shown that in this case we have $n_{A0}' = 1/r, n_{A1}' = -1/r, n_{B1}' = -1, n_{V0}' = -(1 + r)/r, and n_{V1}' = (1 + r)/r$, leading to

$$n_{B0} n_{A0}^{1/r} n_{V0}^{-(1+r)/r} = n_{B1} n_{A1}^{1/r} n_{V1}^{-(1+r)/r} e^{-\delta G/k_B T}.$$
or in terms of mole fractions

\[
\frac{x_{B0}}{x_{A0}} \left( \frac{x_{V0}}{x_{V1}} \right)^{1/x_{B1}} = \frac{x_{B1}}{x_{A1}} \left( \frac{x_{A1}}{x_{V1}} \right)^{1/x_{B1}} e^{-\delta G/k_BT}
\]  \tag{11}

where \(x_{V0} = n_{V0}/(n_{A0} + n_{B0})\) and \(x_{V1} = n_{V1}/(n_{A1} + n_{B1})\). This system is constrained such that if the bulk loses a single solute atom to the interface, it must also lose \(1/r\) solvent atoms to maintain a constant composition, and so gain \((1 + r)/r\) vacancies.

Equation (11) is the central focus of this study. In the following I present numerical solutions and discuss some of its implications.

3 Numerical analysis

To investigate the extent to which the solutions to (1) and (11) differ, I have determined interface compositions \(x_{B0}\) that satisfy equation (11) as a function of bulk composition \(x_{B1}\) for specific values of \(\nu = x_{V0}/x_{V1}\) and \(\delta G/k_BT\) using numerical techniques. Explicitly, I have defined

\[
f(x, y) = y(1 - y)^{(1-x)/x_{V0} - 1/x} \]

\[
- x(1 - x)^{(1-x)/x_{V1} - 1/x} e^{-\delta G/k_BT}
\]

and interpolated to find the set of points \((x_0, y_0)\) such that \(f(x_0, y_0) = 0\). Given \(v_0 = x_{V0}/x_{V1}, v_1 = x_{V1},\) and \(\delta G,\) the points \((x_0, y_0)\) represent solutions to equation (11), with \(y_0 = x_{B0} = \Gamma_0/\Gamma\) for a specified bulk composition \(x_0 = x_{B1}\).

A typical solution set is plotted in Figure 1, for which \(\delta G/k_BT = +1.5\) and \(\nu = 1.0\). In the same figure I have plotted the associated Langmuir-McLean isotherm, labeled \(LM\), as well as the Langmuir-McLean isotherm for \(\delta G/k_BT = -1.5,\) labeled \(LM^{-1}\). It can be seen that across a wide range of compositions the lower curve predicts segregation at rates lower than those of the Langmuir-McLean isotherm. The most striking difference, however, is the appearance of a second branch, as indicated by the blue curve with round bullets. In this figure the second branch tracks \(LM^{-1}\) in the dilute limit. Unlike \(LM\) and \(LM^{-1}\), which correspond to oppositely signed segregation free energies, both red and blue curves represent solutions to equation (11) for \(\delta G/k_BT = +1.5\).

The red curve with square bullets represents a solution with a diminished concentration of solute in the interface than in the bulk \((x_{B0} < x_{B1})\) whereas the blue curve with round bullets represents a solution with augmented solute content in the interface \((x_{B0} > x_{B1})\).

The nature of the isotherm fundamentally alters if the vacancy ratio \(\nu\) differs from unity. I illustrate the dependance on \(\nu\) in Figure 2, where solutions obtained for the same segregation free energy \(\delta G/k_BT = +1.0\) but differing values of \(\nu\) are plotted. Figure (2a) depicts variations that occur for \(\nu \leq 1,\) when the mole fraction of vacancies in the bulk exceeds that in the interface. As \(\nu\) decreases, it can be seen that a gap opens in the upper branch (blue) along the \(x_{B0}\) axis, suggesting a minimal segregation \(x_{B0} \approx 1 - \nu,\) i.e. \(\Gamma_B \approx (v_1 - v_0)/(v_1 + v_0),\) in the dilute limit. The lower branch shifts uniformly downward as \(\nu\) increases, indicating reduced segregation roughly proportional to \(\nu.\)

A system for which the interface vacancy content exceeds the bulk vacancy content \((\nu > 1)\) is depicted in Figure (2b). It can be seen that the upper and lower branches pull away from the origin and merge as \(\nu\) increases, opening up a gap along the \(x_{B1}\) axis in which no potential stable solutions \(x_{B0}\) exist, apart from \(x_{B0} = 0\) or \(x_{B1} = 1.\) Calculations suggest that this gap exists even for small excursions in \(\nu\) above 1.

The solutions to equation (11) exhibit much different behavior than the Langmuir-McLean isotherm under segregation free energy sign reversal. In Figure (3a) I depict two curves obtained for \(\delta G/k_BT = +1.0\) and \(\delta G/k_BT = -1.0,\) both using \(\nu = 0.75.\) Also depicted are the associated Langmuir-McLean isotherms. Whereas the Langmuir-McLean isotherm flips across the diagonal, solutions to equation (11) assume very different forms. Note that the two upper branches yield the same minimal segregation \(x_{B0} \approx 1 - \nu\) as \(x_{B1} \rightarrow 0.\)

The dependance on \(\nu\) for negative segregation free energy solutions is explored in Figure (3b). All of the curves plotted in Figure (3b) were obtained using \(\delta G/k_BT = -1.0,\) except for the curve \(LM,\) which is the Langmuir-
McLean isotherm for $\delta G/k_B T = +1.0$. The curves are labeled with the associated value of $\nu$. As $\nu$ increases toward 1, the isotherm pulls away from the point $(1,1)$ and contracts toward the origin. For $\nu = 1$ the isotherm vanishes. No solutions exist for $\delta G < 0$ and $\nu \geq 1$, apart from $x_{B0} = 0$ or $x_{B0} = 1$.

4 Discussion

To more readily compare equations (1) and (11), note that we can express (11) as

$$\frac{\Gamma_B}{\Gamma_V - \Gamma_B} = \frac{x_B}{x_A} \exp \left[ -\frac{\delta G}{k_B T} + \frac{1}{x_B} \ln \left( \frac{x_A x_V 0}{x_{A0} x_{V1}} \right) \right]$$  \hspace{1cm} (13)

with $\Gamma_V = \Gamma_0/(1 + x_{V0})$ as before. It can be seen from this equation that if the composition and vacancy content are similar in the interface and the bulk, then the ratio inside the logarithm is close to unity, reproducing the original Langmuir-McLean relation. This ratio may be recognized as an approximation to the equilibrium rate constant $k$ for the interaction

$$A_0 + V_1 \overset{k}{\Rightarrow} A_1 + V_0$$  \hspace{1cm} (14)

in which the interface and the bulk exchange component $A$ and vacancies. We would therefore expect $k \approx 1$ when the standard formation energies for vacancies and component $A$ do not differ much between bulk and interface sites. Otherwise, unconditional reduction to the Langmuir-McLean form requires $r = -1$, which is unphysical.

When $k \neq 1$, the numerical analysis presented in the previous section indicates qualitative differences between segregation described by the Langmuir-McLean model and by equation (11). The appearance of two stable states, or complexions, over a broad range of values indicates that there are two different system configurations that can accomodate chemical differences between the interface and the surrounding bulk. The nature of these two configurations is unclear, apart from the fact that one is enriched, and one depleted, in segregated solute, relative to the bulk. From a purely mathematical perspective, these configurations result from the fact that $x(1-x)^{1/r} = C$ can admit two distinct solutions, where $r$ and $C$ are constants.

The appearance of two branches in solutions to equation (11) is not uncommon. Each branch indicates a set of points such that $F'' = 0$. The stability of each state can be determined by evaluating the second derivative $F''$. In the Langmuir-McLean approximation, with $U'' = 0$, we obtain

$$\frac{F''}{k_B T} = \frac{1}{n_{B0}} + \frac{1}{n_{B1}} + \frac{1}{r^2} \left[ \frac{1}{n_{A0}} + \frac{1}{n_{A1}} \right]$$

$$+ \frac{(1+r)^2}{r^2} \left[ \frac{1}{n_{V0}} + \frac{1}{n_{V1}} \right]$$  \hspace{1cm} (15)

from which it follows that both branches represent potentially stable solutions as long as the $\{n_a\}$ are all positive. In a more realistic model, $U'' < 0$ could potentially modify the stability of either branch.

We might instead expect one stable branch and one unstable branch, and so it is important to question whether both branches are physically relevant. Due to the introduction of mole fractions, no mechanism exists in the formalism to guarantee that all component population variables $\{n_a\}$ remain individually positive in the solution. Indeed, negative population variables easily appear as solutions to the traditional Langmuir-McLean equation (1) for most values of $x_B$ once concrete values are specified for the model parameters. In the current model, negative values could lead to $F'' < 0$ in equation (15), resulting in an unphysical solution that appears to be thermodynamically viable.

Therefore let us investigate whether either solution requires negative population variables. At every point along either branch it is clear that $0 < x_{B0} < 1$ and $0 < x_{A0} < 1$, so that $n_{B0}$ and $n_{A0}$ must be either both positive or both negative. Also, $n_{V0}$ must have the same sign as $n_{B0}$ and $n_{A0}$ when we provide an appropriate value for $x_{V0}$ to define the quantity $\Gamma_V = \Gamma_0/(1 + x_{V0})$. The same considerations apply for $n_{A1}$, $n_{B1}$, and $n_{V1}$, except that the sign of $n_{V1}$ is linked to the sign of $n_{V0}$ through the quantity $\nu = x_{V0}/x_{V1}$; only positive values for $\nu$ have been considered in this work. These considerations suggest that all quantities in the solution are either all positive or all negative. But it is clear that equation (11) is invariant under a transformation that inverts the sign of all population variables. If $\{n_a\}$ is a solution,
so is \{-n_\alpha\}. The corresponding mole fractions are positive in both cases and satisfy the same equation.

Each of these branches therefore represents a set of potentially stable, physically relevant solutions to equation (11). As in the Langmuir-McLean case, however, the entire domain is most likely not accessible once concrete parameters have been specified. It seems probable that when the system finds itself in one of these two states, the second state becomes both unphysical and unstable, corresponding to negative \{n_\alpha\} and \(F'' < 0\).

The free energy \(F\) and its derivatives \(F'\) and \(F''\) in the Stirling approximation become difficult to define along the borders, where at least one population variable equals zero. The nature of the limiting behavior of the system at the poles (0,0) and (1,1) clearly influences the shape of the global isotherm. The value of \(\nu\) and the sign of \(\delta G\) appear to control whether the system is attracted or repulsed from these poles, and to what extent. This suggests that the local value of \(\nu\) plays a large role in controlling the dynamics of segregation.

This model may be most appropriate in systems that exhibit a preferred bulk solute content \(x_{B1}\). On the other hand, the constant mole fraction constraint on which it is based is better aligned with the interpretation that it provides the most probable segregation for a specified bulk composition. Regardless of its applicability, the substantial departure observed from Langmuir-McLean behavior indicates the critical role that the vacancy constraint plays in determining the shape of the Langmuir-McLean isotherm.

5 Summary

In this work I have presented a simple modification to the Langmuir-McLean model of grain boundary segregation, leading to equation (11). In contrast to the Langmuir-McLean model, the proposed model allows the interface and the bulk to exchange vacancies as well as atoms to determine the most probable segregation given a specified bulk mole solute content \(x_{B1}\).

Numerical analysis indicates that this modification has a large effect on the predicted segregation. In particular, two complexions appear across a wide range of bulk compositions, corresponding to solute enrichment or deficiency relative to the bulk. The ratio of the vacancy mole fraction in the interface to the vacancy mole fraction in the bulk assumes a prominent role in determining the shape of the isotherm.

Acknowledgements

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

References

[1] P Lejcek, Grain Boundary Segregation in Metals. Springer, Science and Business Media (2010)
[2] AP Sutton and RW Balluffi. Interfaces in Crystalline Materials. Clarendon Press (1995)
[3] R Kirchheim. “Reducing grain boundary, dislocation line and vacancy formation energies by solute segregation. I. Theoretical background.” Acta Mater. 55 (2007) 5129-5128
[4] C Koch, R Scattergood, K Darling, and J Semones. “Stabilization of nanocrystalline grain sizes by solute addition.” J Mater. Sci. 43 (2008) 7264-7272
[5] JW Gibbs, The Collected Works of J. Willard Gibbs, Ph.D, LLD. Yale University Press, London, England, Vol. 1-2 (1957)
[6] AK de Silva, RD Kamachali, D Ponge, B Gault, J Neugebauer, and D Raabe, “Thermodynamics of grain boundary segregation, interfacial spinodal and their relevance for nucleation during solid-solid phase transitions.” Acta Mater 168, 109-120 (2019)
[7] M Kuzmina, D Ponge, and D Raabe. “Grain boundary segregation engineering and austenite reversion turn embrittlement into toughness: Example of a 9 wt. % medium Mn steel.” Acta Mater. 86, 182 (2015)
[8] D. Raabe, M. Herbig, S. Sandlöbes, Y. Li, D. Tytko, M. Kuzmina, D. Ponge, and P.P. Choi. “Grain boundary segregation engineering in metallic alloys: A pathway to the design of interfaces.” Curr Op Solid St and Mat Sci 18 (2014) 253-261
[9] L. Huber, R. Hadian, R. Grabowski, and J. Neubeauer. “A machine learning approach to model solute grain boundary segregation.” npj Comput Mater 4, 64 (2018)
[10] D. McLean, Grain Boundaries in Metals. Clarendon Press (1957)
[11] I. Langmuir, “The adsorption of gases on plane surfaces of glass, mica, and platinum.” J. Am. Chem. Soc., 40(9), 1361-1403 (1918)
[12] RH Fowler and EA Guggenheim, Statistical thermodynamics. Cambridge University Press (1939)
[13] MP Seah and ED Hondros, “Grain boundary segregation.” Proc. Roy. Soc. Lond. A 335, 191 (1973)
[14] P Wynblatt and D Chatain. “Anisotropy of segregation at grain boundaries and surfaces.” Metall Mater Trans A 37 (2006) 2595-2620
Figure 1: The segregation ratio $x_B = \Gamma_B/\Gamma_V$ as predicted by equation (11) for segregation free energy $\delta G = +1.5k_B T$, plotted versus mole fraction of bulk solute $x_{B_1}$, with equal vacancy mole fractions in the bulk and in the interface ($x_{V_0} = x_{V_1}$). The Langmuir-McLean isotherms for $\delta G = +1.5k_B T$ and $\delta G = -1.5k_B T$ are labeled $LM$ and $LM^{-1}$, respectively. All curves are vacancy-normalized, with $\Gamma_V = \Gamma_0/(1+x_{V_0})$. Both upper and lower curves are solutions to equation (11) for $\delta G = +1.5k_B T$. With each value $x_{B_1}$ is associated two possible stable compositions, or complexions: one on the blue curve and one on the red curve.
Figure 2: Dependence on vacancy content ratio. The segregation ratio \( x_{B0} = \Gamma_B / \Gamma_V \) as predicted by equation (11), plotted for several values of \( \nu = x_{V0}/x_{V1} \). All curves in both (a) and (b) represent grain boundaries with segregation free energy \( \delta G = k_B T \) and are labeled with an associated value of \( \nu \). The curve labeled \( LM \) is the Langmuir-McLean isotherm for \( \delta G = + k_B T \), and the curve labeled \( LM^{-1} \) is the Langmuir-McLean isotherm for \( \delta G = - k_B T \). (a) \( \nu = 1.0, \nu = 0.75, \) and \( \nu = 0.5 \). Each value admits an upper and a lower branch. (b) \( \nu = 1.0, \nu = 1.2, \) and \( \nu = 1.5 \). The two branches merge and pull away from \((0,0)\) for \( \nu > 1 \).

Figure 3: Negative segregation free energy. The segregation ratio \( x_{B0} = \Gamma_B / \Gamma_V \) as predicted by equation (11) plotted for several values of \( \delta G < 0 \). The curve labeled \( LM \) is the Langmuir-McLean isotherm. The curve labeled \( LM^{-1} \) is the Langmuir-McLean isotherm for \( \delta G = - k_B T \). (a) Comparison between solutions obtained for \( \delta G = + k_B T \) and \( \delta G = - k_B T \). Both solutions have been obtained assuming \( \nu = 0.75 \). In the negative energy case the upper and lower branches have merged to form the small inner half-loop about the origin. (b) Three curves with \( \delta G = - k_B T \) but different values of \( \nu \). As \( \nu \) increases the upper and lower branches pull away from the \((1,1)\) and merge. The curves vanish for \( \nu \geq 1 \).