J. Min. Metall. Sect. B-Metall., 56 (2) B (2020) 183 - 191

**Journal of Mining and Metallurgy,
Section B: Metallurgy**

AN EFFECTIVE ALGORITHM TO IDENTIFY THE MISCIBILITY GAP IN A BINARY SUBSTITUTIONAL SOLUTION PHASE

T. Fu[a], Y. Du [b,*], Z.-S. Zheng [a,*], Y.-B. Peng [c], B. Jin [b], Y.-L. Liu [b], C.-F. Du [a], S.-H. Liu [b], C.-Y. Shi [b], J. Wang [b]

[a*] School of Mathematics and Statistics, Central South University, Changsha, Hunan, China
[b] State Key Laboratory of Powder Metallurgy, Central South University, Changsha, Hunan, China
[c] College of Metallurgy and Materials Engineering, Hunan University of Technology, Zhuzhou, Hunan, China

(Received 16 September 2019; accepted 18 May 2020)

Abstract

In the literature, no detailed description is reported about how to detect if a miscibility gap exists in terms of interaction parameters analytically. In this work, a method to determine the likelihood of the presence of a miscibility gap in a binary substitutional solution phase is proposed in terms of interaction parameters. The range of the last interaction parameter along with the former parameters is analyzed for a set of self-consistent parameters associated with the miscibility gap in assessment process. Furthermore, we deduce the first and second derivatives of Gibbs energy with respect to composition for a phase described with a sublattice model in a binary system. The Al-Zn and Al-In phase diagrams are computed by using a home-made code to verify the efficiency of these techniques. The method to detect the miscibility gap in terms of interaction parameters can be generalized to sublattice models. At last, a system of equations is developed to efficiently compute the Gibbs energy curve of a phase described with a sublattice model.

Keywords: *Computational thermodynamics; Equilibrium calculations; Phase diagram; Miscibility gap; Algorithm*

1. Introduction

Miscibility gap occurs when a two-phase coexistence line in a phase diagram ends at a critical point [1]. On one hand, miscibility gap has been well understood and extensively used to develop high-performance materials through the spinodal-type decomposition of the microstructure, such as (Ti,Zr)C [2, 3], TiAlN [4], etc. On the other hand, for some alloys like high-entropy alloys, intermediate phase or miscibility gap should be avoided in order to form a single-phase microstructure thereby obtaining excellent performance. As a result, it is of great importance to acquire the information about miscibility gap of materials during the developing process. In the literature, many authors presented mathematic equations for understanding miscibility gap in terms of Gibbs energies [5-8], and numerically detected them by a discretization of composition axis [9-13]. To the best of our knowledge, however, there is no detailed description about how to detect if a miscibility gap exists in terms of interaction parameters analytically. One purpose of this paper is to develop a novel method to determine the existence of miscibility gap analytically for given thermodynamic parameters. In addition, the ranges of interaction parameters are analyzed mathematically in the solution model. The other objective in the present work is to provide a new approach to calculate the miscibility gap and guide selection for the interaction parameters during the thermodynamic assessment in binary systems.

In section 2, we present a simple method to identify if there is a miscibility gap in terms of the interaction parameters analytically. Subsequently, in order to investigate the existence of the miscibility gap, we deduce the first and second derivatives of Gibbs energy with respect to composition for a phase described with a sublattice model in section 3 and section 4. After that in section 5, the calculations of the Al-Zn and Al-In phase diagrams are demonstrated to show the unique features of the presently developed new algorithm. Finally, a summary is made in section 6. It could be mentioned that the outcome of the present work is of both scientific and educational interests.

2. On the existence of miscibility gap in view of interaction parameters

In thermodynamic equilibrium calculations, if the miscibility gap exists it should be considered. In this

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Corresponding author: yong-du@csu.edu.cn; zszheng@csu.edu.cn

https://doi.org/10.2298/JMMB190916004F

section, we will investigate the existence of the miscibility gap in a binary phase with a substitutional solution model.

For fixed T and P, let $1-x$ and x be the molar fractions of components A and B, respectively. Then, the molar Gibbs energy of a phase described with a substitutional solution model can be expressed as

$$G_M = (1-x)G_A^0 + xG_B^0 + RT\left[(1-x)\ln(1-x) + x\ln x\right] + (1-x)x\sum_{i=0}^{n}(1-2x)^i L_i \tag{1}$$

where G_A^0 (respectively, G_B^0) is the Gibbs energy of pure A (respectively, B). $L_i\ (0 \le i \le n)$ are the interaction energy parameters between A and B.

Generally, a miscibility gap involves phase separation within a single phase. The corresponding Gibbs energy curve for fixed T shows two coexisting compositions and two inflection points, except for the consolute point [1], cf. Fig. 1. Mathematically, this implies that there are two real number solutions to equation $G''_M(x) = 0$ in interval (0, 1). Here the second order derivative of G_M with respect to x is given by

$$G''_M = \frac{RT}{x(1-x)} - 2L_0 + (12x-6)L_1 + \left(-48x^2 + 48x - 10\right)L_2 + \cdots \tag{2}$$

We now discuss the existence of the miscibility gap with the increase in the number of the interaction parameters.

2.1 Case $n = 0$

For the case $L_0 \ne 0$ and $L_i = 0\ (i \ge 1)$, by expression (2), equation $G''(x) = 0$ can be expressed as:

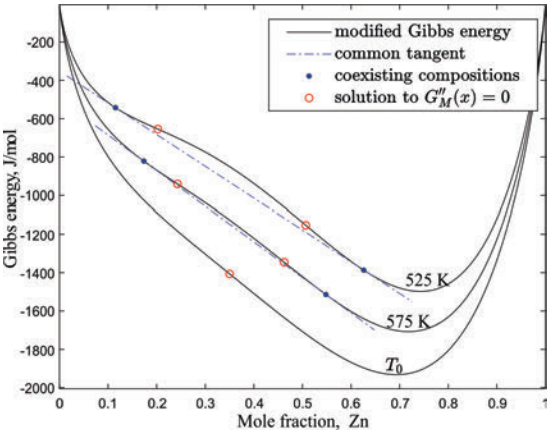

Figure 1. *Modified Gibbs energy curves after a linear shifting, $G_M - G_{Al}^0(1-x) - G_{Zn}^0 x$, at different temperatures in Al-Zn binary system. The curve at T_0 = 625.7111 K shows the Gibbs energy related to the consolute point while equation $G''_M(x) = 0$ has only one solution*

$$\frac{RT}{2L_0} = x(1-x) \tag{3}$$

It is obvious that Eq. (3) has two solutions in interval (0, 1) only if $0 < \frac{RT}{2L_0} < \frac{1}{4}$. In other words, there exists a miscibility gap in this phase when $L_0 > 2RT$.

2.2 Case $n = 1$

Similarly, for the case $L_1 \ne 0$ and $L_i = 0\ (i \ge 2)$, the equation $G''(x) = 0$ is equivalent to

$$RT = x(x-1)(12L_1 x - 6L_1 - 2L_0) \tag{4}$$

Let $h(x)$ denote the right hand side of Eq. (4). It should be noted that there exist two real solutions to Eq. (4) if and only if the maximum of $h(x)$ in interval (0, 1) is greater than RT. The function $h(x)$ is a cubic polynomial and has three zero points, 0, 1 and $\frac{3L_1 + L_0}{6L_1}$. This indicates that equation $h'(x) = 0$ has two solutions $x_1, x_2\ (x_1 < x_2)$ where $h'(x)$ is the first order derivative of $h(x)$ and

$$h'(x) = 36L_1 x^2 - (36L_1 + 4L_0)x + 6L_1 + 2L_0 \tag{5}$$

Thanks to the feature of the cubic function, there are only two cases such that $\max_{x\in(0,1)} h(x) > 0$, namely,

$$\max_{x\in(0,1)} h(x) = \begin{cases} h(x_1), & if\ L_1 > 0\ and\ \dfrac{3L_1 + L_0}{6L_1} > 0, \\ h(x_2), & if\ L_1 < 0\ and\ \dfrac{3L_1 + L_0}{6L_1} < 1 \end{cases} \tag{6}$$

We are now in a position to construct the judgement for the existence of the miscibility gap according to $L_1 > 0$ or $L_1 < 0$. For $L_1 > 0$, if $3L_1 + L_0 > 0$ and $h(x_1) > RT$, there is a miscibility gap in this phase, while for $L_1 < 0$, if $3L_1 - L_0 < 0$ and $h(x_2) > RT$, the miscibility gap exists in this phase.

When dealing with the miscibility gap in assessment process, to evaluate a set of self-consistent parameters, the last interaction parameter should be reasonably selected on the basis of former interaction parameters. In fact, if $L_0 > 2RT$, since $G''_M(0.5) = 4RT - 2L_0 < 0$ and the fact that $G''_M \to +\infty$ as $x \to 0$ or $x \to 1$, equation $G''_M(x) = 0$ always has two solutions in interval (0, 1) no matter what value the parameter L_1 takes, i.e., there is always a miscibility gap in this phase.

On the other hand, if $L_0 < 2RT$, we rewrite Eq. (4) as

$$\frac{RT}{x(x-1)} + 2L_0 = (12x-6)L_1 \tag{7}$$

The functions from the both sides of Eq. (7) are plotted against x in Fig. 2, we can observe that when $L_1 = L_1^0$, only one value x_0 satisfies Eq. (7), where x_0 and L_1^0 can be computed by

$$\begin{cases} \dfrac{RT}{x_0(x_0-1)} + 2L_0 = (12x_0-6)L_1^0 \\ \dfrac{RT(1-2x_0)}{x_0^2(x_0-1)^2} = 12L_1^0 \end{cases} \qquad (8)$$

Hence, we can conclude that if $L_1 > L_1^0$ or $L_1 < -L_1^0$, Eq. (7) has two solutions in interval (0, 1), namely, there will exist a miscibility gap in this phase.

2.3 Case $n \geq 2$

The analysis described in sections 2.1 and 2.2 would be complex and expensive for the case $L_n \neq 0\,(n \geq 2)$ and $L_i = 0\,(i \geq n+1)$. Therefore, a numerical method for finding the solutions of polynomial will be employed here. Rewrite the equation $G''_M(x) = 0$ as

$$x(x-1)\begin{Bmatrix} -2L_0 + (12x-6)L_1 + \\ (-48x^2+48x-10)L_2 + \cdots \end{Bmatrix} - RT = 0 \qquad (9)$$

It is easy to check that the function from the left side of Eq. (9) is a polynomial of degree $n+2$. By computing the eigenvalues of the corresponding companion matrix [17], if there are at least two real eigenvalues in interval (0,1), a miscibility gap exists; otherwise, it does not exist.

Generally, in a binary system, a substitutional solution model is considered with no more than 4 interaction parameters, i.e.,$n \leq 3$, and mostly we just take $n = 2$. In thermodynamic assessment process, according to previously introduced interaction parameters, we can compute the range of the last interaction parameter in which a miscibility gap exists. Now consider the case $n = 2$ and rewrite Eq. (9) as

$$\frac{RT}{x(x-1)} + 2L_0 + (48x^2-48x+10)L_2 = (12x-6)|L_1| \qquad (10)$$

where the left hand side is a function symmetry with respect to $x = \frac{1}{2}$, and for different L_2 the corresponding function curves invariably pass through the point $\left(\frac{6-\sqrt{6}}{12}, 2L_0 - \frac{24RT}{5}\right)$, as shown in Fig. 3. In Eq. (10), by taking $x = \frac{6-\sqrt{6}}{12}$, the right hand side becomes $-\sqrt{6}|L_1|$. Thus, if $2L_0 - \frac{24RT}{5} > -\sqrt{6}|L_1|$, there is always a miscibility gap in this phase whatever the parameter L_2 takes.

If $2L_0 - \frac{24RT}{5} < -\sqrt{6}|L_1|$, it can be observed from Fig. 3 that when taking $L_2 = L_{2,1}^0$ or $L_2 = L_{2,2}^0$, Eq. (10) has only one solution $x_{0,1}$ or $x_{0,2}$, respectively. These two sets of values $L_{2,1}^0$, $x_{0,1}$ and $L_{2,2}^0$, $x_{0,2}$ can be obtained by solving Eq. (11) of unknowns L_2^0, x_0:

$$\begin{cases} \dfrac{RT}{x_0(x_0-1)} + 2L_0 + \\ (48x_0^2 - 48x_0 + 10)L_2^0 = (12x_0-6)|L_1| \\ \dfrac{RT(1-2x_0)}{x_0^2(x_0-1)^2} + 48L_2^0(2x_0-1) = 12|L_1| \end{cases} \qquad (11)$$

Thus, if $L_2 > L_{2,1}^0$ or $L_2 < L_{2,2}^0$, there exists a miscibility gap in the phase.

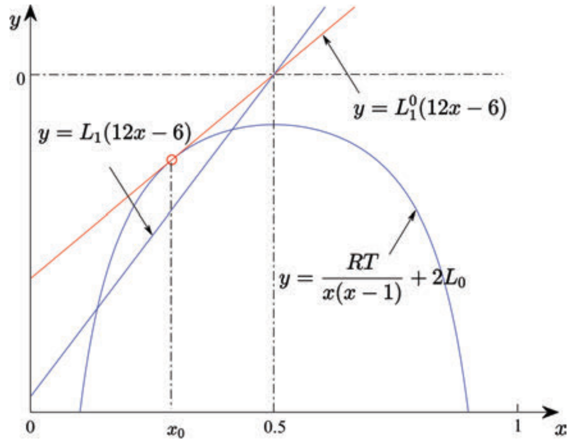

Figure 2. Geometric illustration for Eq. (7)

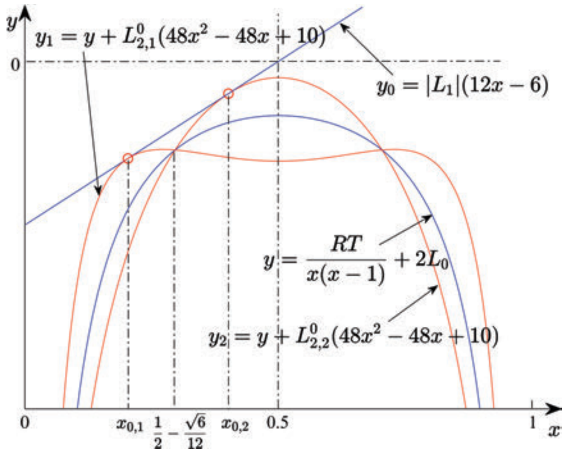

Figure 3. Geometric illustration for Eq. (11)

It is remarkable that since the analysis for the existence of miscibility gap in this section is in terms of interaction parameters at different discrete values of temperature, the present approach can also be used to check the existence of the miscibility gaps for different expressions of *T*-dependence of interaction parameters [14-16] quickly and efficiently.

In addition, for the linear model for the *T*-dependence of interaction parameters, generally given by $L_i = a_i + b_i T$, Kaptay described that for the simplest case of *n = 0* an artificial inverted miscibility gap appears at high temperature when $a_0 < 0$ and $b_0 > 2R$ [15]. In fact, this simple rule can be used for the case of *n = 1* due to the fact that if $b_0 > 2R$, there always holds $G''_M(0.5) = 4RT - 2L_0 < 0$ at high temperature no matter what value L_1 is.

Furthermore, for the case *n = 2*, according to the discussion about Eq. (10) and Fig. 3, we find that if $2L_0 - \frac{24RT}{5} > -\sqrt{6}\left|L_1\right|$, a miscibility gap appears regardless of the value of L_2. Since the parameter $L_i(T)$ can be approximated by $b_i T$ at sufficiently high temperatures, we have $2b_0 T - \frac{24RT}{5} > -\sqrt{6}\left|b_1\right| T$. This implies that an artificial inverted miscibility gap arises if $5\left(2b_0 + \sqrt{6}\left|b_1\right|\right) > 24R$, or roughly, $b_0 > 12R/5$. On the other hand, the function from the right side of Eq. (10) always passes though the point (1/2, 0), and when taking $x =$ 1/2, the left side in Eq. (10) is equal to $2L_0 - 2L_2 - 4RT$Analogous to the analysis above, in view of Fig. 3, when $2L_0 - 2L_2 - 4RT > 0$, i.e. $b_0 - b_2 > 2R$, an artificial inverted miscibility gap appears at high temperatures.

3. Finding the miscibility gap for a phase described with a sublattice model

The method descried in section 2 deals with a phase described with a substitutional solution model. Next we consider a sublattice model in which the corresponding Gibbs energy can also be expressed by a function of two variables, such as phase *η* in the Zr-Sn [18] binary system, which is described with the sublattice model $(Zr)_5(Sn)_3(Sn,Va)_1$. Let $y_{Sn}, y_{Va}\left(y_{Sn} + y_{Va} = 1\right)$ be the site fractions of the third sublattice for phase *η*. The molar fractions of components Sn and Zr are

$$x_{Sn} = \frac{3 + y_{Sn}}{9 - y_{Va}} \text{ and } x_{Zr} = \frac{5}{9 - y_{Va}} \tag{12}$$

Then the corresponding Gibbs energy expression reads:

$$G_M = \left[\begin{array}{l} y_{Sn}G(\eta, Zr:Sn:Sn;0) + y_{Va}G(\eta, Zr:Sn:Va;0) + \\ RT\left(y_{Sn}\ln y_{Sn} + y_{Va}\ln y_{Va}\right) \\ + y_{Sn}y_{Va}L(\eta, Zr:Sn:Sn,Va;0) + \\ y_{Sn}y_{Va}(y_{Sn} - y_{Va})L(\eta, Zr:Sn:Sn,Va;0) \end{array}\right] \Big/ \left(9 - y_{Va}\right). \tag{13}$$

In this section, we shall study the existence of the miscibility gap for a phase described with a sublattice model under fixed *T* and *P* where the Gibbs energy expression involves two internal variables y_B, y_{Va} or y_A, y_B :

$$G_M = \frac{G\left(y_B, y_{Va}\right)}{a - y_{Va}} \text{ or } G_M = \frac{G\left(y_A, y_B\right)}{a} \tag{14}$$

where constant *a* is the sum of the numbers of sites for all sublattices, and bivariate function *G* has the same form as expression (1). We next focus on the case of y_B, y_{Va} . The case of y_A, y_B is similar to that of y_B, y_{Va}. To this end, we start by deducing the first and second derivatives of G_M with respect to *x*.

Generally, the mole fraction of element B in that phase is defined by

$$x = \frac{a_B + y_B}{a - y_{Va}} = \frac{a_B + y_B}{a - 1 + y_B} = 1 - \frac{a - 1 - a_B}{a - 1 + y_B} \tag{15}$$

Here Eq. (15) follows from the relation $y_B + y_{Va} = 1$, and a_B is a constant and can be zero. Then G_M is regarded as a function of *x*:

$$G_M = \bar{G}\left(y_B(x)\right) = \frac{G\left(y_B, y_{Va}\right)}{a - 1 + y_B} \tag{16}$$

Consequently, we obtain the first derivative of G_M with respect to *x* as:

$$\frac{dG_M}{dx} = \frac{d\bar{G}}{dy_B}\frac{dy_B}{dx} = \frac{\left(\frac{\partial G}{\partial y_B} - \frac{\partial G}{\partial y_{Va}}\right)\left(a - 1 + y_B\right) - G}{\left(a - 1 + y_B\right)^2}\frac{dy_B}{dx} \tag{17}$$

From the relation (15), there holds that

$$\frac{dx}{dy_B} = \frac{a - 1 - a_B}{\left(a - 1 + y_B\right)^2} \tag{18}$$

Thus, we arrive at

$$\frac{dG_M}{dx} = \frac{d\bar{G}}{dy_B}\frac{dy_B}{dx} = \frac{\left(\frac{\partial G}{\partial y_B} - \frac{\partial G}{\partial y_{Va}}\right)\left(a - 1 + y_B\right) - G}{a - 1 + a_B} \tag{19}$$

Similarly, we get the following second derivative:

$$\begin{aligned} \frac{d^2G_M}{dx^2} &= \frac{1}{\left(a - 1 + a_B\right)}\frac{d}{dy_B}\left(\begin{array}{c}\left(\frac{\partial G}{\partial y_B} - \frac{\partial G}{\partial y_{Va}}\right)\cdot \\ \left(a - 1 + y_B\right) - G\end{array}\right)\frac{dy_B}{dx} \\ &= \left(\frac{\partial^2 G}{\partial {y_B}^2} - 2\frac{\partial^2 G}{\partial y_B \partial y_{Va}} + \frac{\partial^2 G}{\partial {y_{Va}}^2}\right)\frac{\left(a - 1 + y_B\right)^3}{\left(a - 1 + a_B\right)^2} \end{aligned} \tag{20}$$

By taking $y_{Va} = 1 - y_B$, it is easily verified that the term $\frac{\partial^2 G}{\partial {y_B}^2} - 2\frac{\partial^2 G}{\partial y_B \partial y_{Va}} + \frac{\partial^2 G}{\partial {y_{Va}}^2}$ has the same expression as Eq. (2). From the discussion in section 2, we know when the miscibility gap exists, there are two real number solutions to equation $G''_M(x) = 0$ in interval (0,1). Noting that $\frac{(a-1+y_B)^3}{(a-1+a_B)^2} \neq 0$, we can conclude that the method described in section 2 works equally well in the case of a sublattice model.

The phase η in Zr-Sn [18] binary system is used as an example to verify the correctness of these derivatives. Here we take $y_B = y_{Sn}$, and set a temperature $T = 1200\ K$ and a number of axis subdivisions $N = 50$. In Fig. 4 we find that the first and second derivatives computed directly by the expressions (19) and (20) coincide with those calculated numerically by the finite difference approximation schemes.

4. The derivatives in a sublattice model

In this section, we shall expand the derivation method introduced in section 3 to a general sublattice model. These derivatives can help to obtain the Gibbs energy curve efficiently by a simple Newton algorithm.

In order to make it easier to understand the derivation for the derivatives of G_M with respect to x, a phase described with $(A,B)_a(A,B)_b$ is taken as an example. Let y'_A, y'_B and y''_A, y''_B denote the constituent fractions of the first and second sublattices, respectively. Then we have

$$x = \frac{ay'_B + by''_B}{a+b} \tag{21}$$

Under fixed T and P, G_M is considered as a function of y'_B and y''_B since $y'_A + y'_B = 1$ and $y''_A + y''_B = 1$. Together with Eq. (21), G_M can also be regarded as a function of y'_B and x, that is,

$$G_M(y'_A, y'_B, y''_A, y''_B) = \hat{G}_M(y'_B, y''_B(y'_B, x)) \tag{22}$$

Thus we can express the partial derivative of G_M with respect to x,

$$\frac{\partial G_M}{\partial x} = \frac{\partial \hat{G}_M}{\partial x} = \frac{\partial \hat{G}_M}{\partial y''_B}\frac{\partial y''_B}{\partial x} = \left(\frac{\partial G_M}{\partial y''_B} - \frac{\partial G_M}{\partial y''_A}\right)\frac{\partial y''_B}{\partial x} \tag{23}$$

Similarly, we have

$$\frac{\partial G_M}{\partial x} = \left(\frac{\partial G_M}{\partial y'_B} - \frac{\partial G_M}{\partial y'_A}\right)\frac{\partial y'_B}{\partial x} \tag{24}$$

Clearly, there holds that for any x,

$$\left(\frac{\partial G_M}{\partial y'_B} - \frac{\partial G_M}{\partial y'_A}\right)\frac{\partial y'_B}{\partial x} = \left(\frac{\partial G_M}{\partial y''_B} - \frac{\partial G_M}{\partial y''_A}\right)\frac{\partial y''_B}{\partial x} \tag{25}$$

In fact, Eq. (25) can also be obtained from the partial Gibbs energies of the end-members in [19, 20]. Applying the end-members (A:A) and (A:B) yields

$$G_{A:A} = G_M + \frac{\partial G_M}{\partial y'_A} + \frac{\partial G_M}{\partial y''_A} - (y'_A, y'_B, y''_A, y''_B)\cdot \left(\frac{\partial G_M}{\partial y'_A}, \frac{\partial G_M}{\partial y'_B}, \frac{\partial G_M}{\partial y''_A}, \frac{\partial G_M}{\partial y''_B}\right)^T \tag{26}$$

$$G_{A:B} = G_M + \frac{\partial G_M}{\partial y'_A} + \frac{\partial G_M}{\partial y''_B} - (y'_A, y'_B, y''_A, y''_B)\cdot \left(\frac{\partial G_M}{\partial y'_A}, \frac{\partial G_M}{\partial y'_B}, \frac{\partial G_M}{\partial y''_A}, \frac{\partial G_M}{\partial y''_B}\right)^T \tag{27}$$

Note that the partial Gibbs energies of the end-members are related to the chemical potentials of the

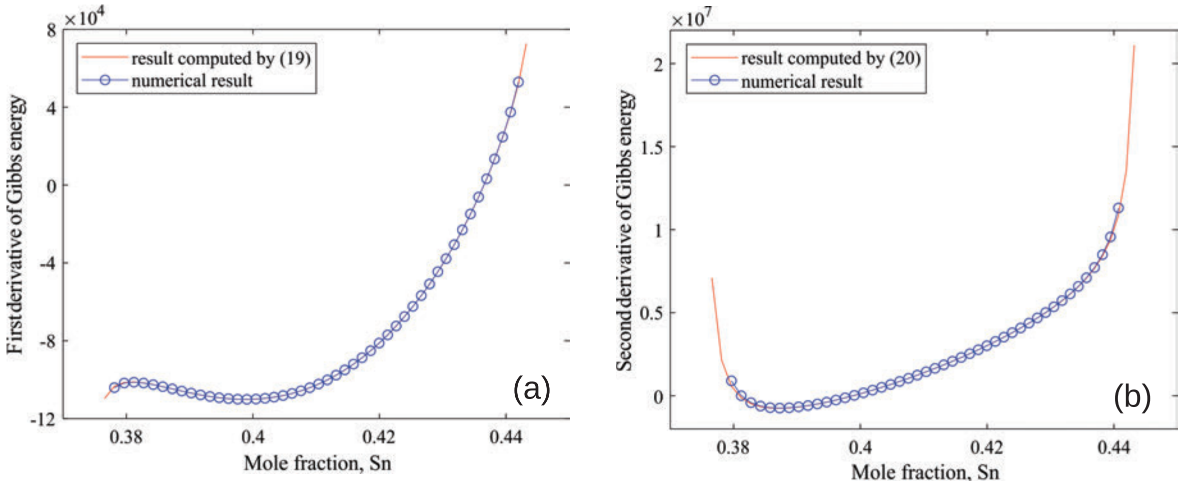

Figure 4. *The first (a) and second (b) derivatives of G_M of phase η at $T = 1200$ K in Zr-Sn system computed directly via formulas (19), (20) and numerically by finite difference schemes*

elements, $G_{A:A} = a\mu_A + b\mu_A$ and $G_{A:B} = a\mu_A + b\mu_B$. Thus we deduce that

$$\frac{\partial G_M}{\partial x} = \mu_B - \mu_A = \frac{1}{b}\left(G_{A:B} - G_{A:A}\right) = \frac{1}{b}\left(\frac{\partial G_M}{\partial y''_B} - \frac{\partial G_M}{\partial y''_A}\right) \quad (28)$$

Analogously, by using the end-members (A:A) and (B:A), there consequently holds that

$$\frac{\partial G_M}{\partial x} = \frac{1}{a}\left(\frac{\partial G_M}{\partial y'_B} - \frac{\partial G_M}{\partial y'_A}\right) = \frac{1}{b}\left(\frac{\partial G_M}{\partial y''_B} - \frac{\partial G_M}{\partial y''_A}\right) \quad (29)$$

It is obvious that Eq. (25) and Eq. (29) are equivalent.

For a given x, we now have 4 equations of 4 unknowns y'_A, y'_B, y''_A, y''_B as follows:

$$\begin{cases} \frac{1}{a}\left(\frac{\partial G_M}{\partial y'_B} - \frac{\partial G_M}{\partial y'_A}\right) = \frac{1}{b}\left(\frac{\partial G_M}{\partial y''_B} - \frac{\partial G_M}{\partial y''_A}\right) \\ x = \frac{a y'_B + b y''_B}{a+b} \\ y'_A + y'_B = 1 \\ y''_A + y''_B = 1 \end{cases} \quad (30)$$

Eq. (30) can be solved by the simple Newton method.

Now we take the phase Cu_2Mg described with $(Cu,Mg)_2(Cu,Mg)_1$ in Cu-Mg [21] binary system as an example to observe the efficiency of Eqs. (23), (24) and (30). At $T = 1000K$, let $N = 100$ be the number of x axis partitions. In Fig. 5(a), the values of Gibbs energy at each node by solving Eqs. (30) with Newton method (denoted by G_M^n) are close to those calculated by traditional discretization method (denoted by G_M^d). In the discretization method, the value of Gibbs energy at any discrete node x_i is approximately obtained by computing the minimum of Gibbs energies at all the gridpoints with the number of internal variable axis subdivisions N`= 1000. Such calculations are time-consuming, in particular for a multi-component phase. And in the Newton method, there are just 10 iterations at each node x_i. In Table 1, for a fixed $N = 100$, we present the maxima of the differences of the above two Gibbs energies at all nodes against various N`. As shown in Table 1, the computation time from the present algorithm is much shorter than that due to the discretization method.

In Fig. 5(b), the first derivatives computed by Eq. (23), equal to those by Eq. (24), nearly coincide with the results calculated by the finite difference method. And the maximum of the differences of the results by Eq. (24) (denoted by $\bar{G}'_M$) and the finite difference method (denoted by $\hat{G}'_M$) is nearby line $x = 1/3$. In Table 2, the maxima of those differences near line $x = 1/3$ are presented against various N.

Table 1. *The maxima of $\left|G_M^n - G_M^d\right|$ and the computation times of the discretization method against different N`. Since the Newton method is independent of the number of subdivisions $N$`, the computation time does not change*

N`	Max $\left\|G_M^n - G_M^d\right\|$	Computation time of discretization method	Computation time of Newton method
1000	51.5938	0.0198 s	0.0003 s
2000	23.8303	0.0263 s	
5000	8.5057	0.0407 s	
10000	3.8669	0.0605 s	
100000	0.259	0.4217 s	

Table 2. *The maxima of $\left|\bar{G}'_M - \hat{G}'_M\right|$ against different N*

N	1000	2000	5000	10000	100000
Max $\left\|\bar{G}'_M - \hat{G}'_M\right\|$	162.1459	41.7066	6.724	1.6499	0.0029

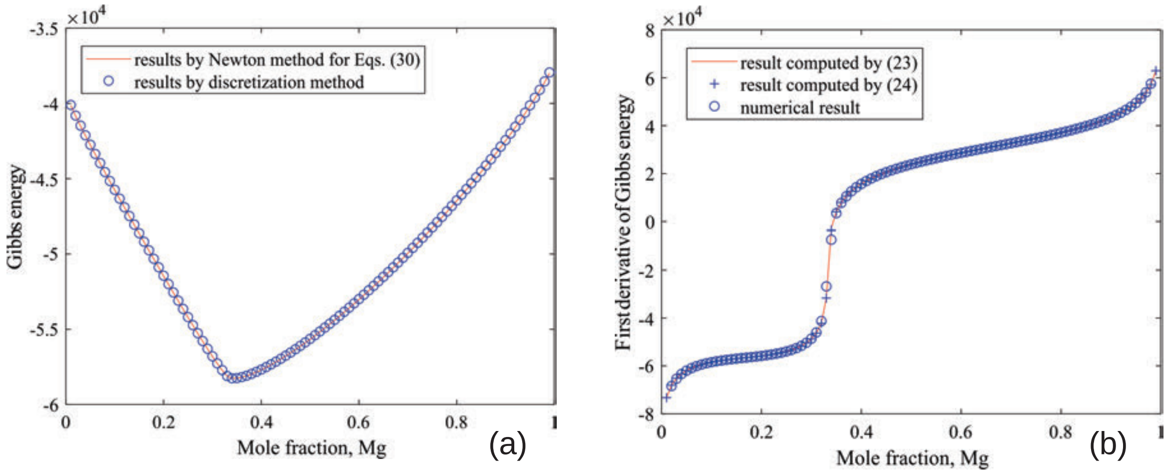

Figure 5. *The Gibbs energies (a) and the first derivatives (b) of the G_M of Cu_2Mg phase at $T = 1000K$ in Cu-Mg system computed by present methods and general numerical methods*

5. Results and discussion

Some numerical results are presented to verify the efficiency of the proposed algorithm in section 2. By using the method described in section 2 to find the existence of the miscibility gap in a phase described with a substitutional solution model, the Al-Zn [22] and Al-In [23] binary phase diagrams are computed with a home-made MATLAB code. The corresponding procedure to calculate binary phase diagrams is described in detail in our recent work [24]. It is stressed that in the calculation of this phase diagram, after finding a miscibility gap in a phase, one still needs to check whether it is the global equilibrium or not. In the calculation of Fig. 6(a), we can easily find the miscibility gap in phase fcc_a1 with the interaction parameters, instead of the discretization of composition axis. And in Fig. 6(b) the miscibility gap exists in the liquid phase.

The parameters L_0, L_1 and L_2 for fcc_a1 phase in the Al-Zn and liquid in the Al-In system are given in Table 3. By inserting L_0, L_1 into Eq. (11), we can calculate the range for L_2 where a miscibility gap exists in this phase.

At $T = 625K$, using Eq. (11), it shows that only when $L_2 < -994.14$ or $L_2 > 1292.17$ a miscibility gap can exist in phase fcc_a1 for the Al-Zn system. The value of L_2 given in the Al-Zn system is within that range, which coincides with the fact that there is a miscibility gap in phase fcc_a1 at 625 K.

On the contrary, at $T = 626$ K, it can be seen that the value of L_2 in the fcc_a1 phase of the Al-Zn system is outside the range resulting from Eq. (11); also, there is no miscibility gap in phase fcc_a1 at this temperature. In addition, except for the solid phase, this method can also be applied to the liquid phase in the Al-In system.

Analogously, the parameters L_0, L_1 for η phase in the Zr-Sn system are given in Table 4. By inserting L_0 into Eq. (9), we calculate the range for L_1 where a miscibility gap exists. At $T = 1340K$, using Eq. (8), we find that only when $L_1 < -28772$ or $L_1 > 28772$ a miscibility gap can exist in phase η. The value of L_1 given in the Zr-Sn system is within that range. At $T = 1341$ K, the value of L_1 is outside the range computed from Eq. (8). And there is no miscibility gap in phase η at this temperature.

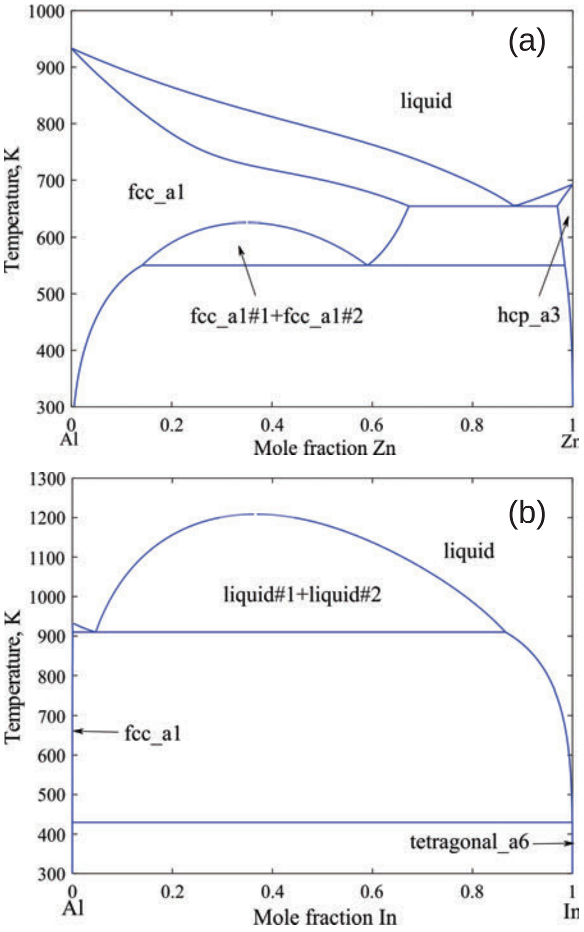

Figure 6. *Al-Zn (a) and Al-In (b) phase diagrams computed by the present algorithm via MATLAB*

Table 4. *Parameters L_0 and L_1 are given in the corresponding TDB file at these temperatures. And L_1 parameter from Eq. (8) is solved with the given L_0*

Phase	T	L_0	Results from Eq.(9)	L_2
η (Zr-Sn)	1340	-17520	< - 28772 > 28772	-28780
	1341	-17548	< -28801 > 28801	-28747

Table 3. *Parameters L_0, L_1 and L_2 are given in the corresponding TDB file at these temperatures. And L_2 parameter from Eq. (11) is solved with the given L_0, L_1*

Phase	T	L_0	L_1	Results from Eq.(11)	L_2
fcc_a1 (Al-Zn)	625	7594.45	3743.46	< - 994.14 >1292.17	-1030.73
	626	594.92	3738.87	< -1042.02 >1344.52	-1027.42
liquid (Al-In)	1208	20670.85	2393.88	< 1675.25 >5021.26	1652.19
	1209	20670.36	2392.68	< 1641.15 >5063.49	1649.02

Table 5. *Implication and guidance to thermodynamic calculations and optimization from the analytical results to identify if a miscibility gap exists for a binary phase* [a]

n	An analytical equation	Implication and guidance
0	$\frac{RT}{2L_0} = x(1-x)$	$L_0 > 2RT$: there is a miscibility gap.
1	$h(x) = RT$ $h(x) := x(x-1)(12L_1x - 6L_1 - 2L_0)$	(1)$L_1 > 0, 3L_1 + L_0 > 0$ and $h(x_1) > RT$, there is a miscibility gap. (2) $L_1 < 0, 3L_1 - L_0 < 0$ and $h(x_2) > RT$, there is a miscibility gap.
≥ 2	$x(x-1)\left[-2L_0 + (12x-6)\ L_1 + (-48x^2 + 48x - 10)L_2 + \cdots\right] - RT = 0$	Solved by Eigenvalue method. If there are at least two real roots in interval (0,1), a miscibility gap exists.

[a] Excess Gibbs energy is given as follows: ${}^{ex}G = x(1-x)\sum_{i=0}^{n}(1-2x)^i L_i$

The outcome of the present work is of interest for the thermodynamic optimization in which a miscibility gap is involved. During the thermodynamic optimization of a binary system in which a miscibility gap exists, Eq.(8) and Eq.(11) can be used to detect numerical regions of the interaction parameters very easily, which will reduce the amount of work for assessments. As a summary, Table 5 presents the implication and guidance to thermodynamic calculations and optimizations from the analytical results for each of the cases n = 0, 1, 2 and > 2.

To the best of our knowledge, no detailed description is presented in textbooks on how to identify if a miscibility gap exists in terms of the given thermodynamic parameters analytically in a binary system. The present work shows all of the details in order to detect the existence of the miscibility gap in a binary system, being of interest to undergraduates and graduates.

6. Summary

In this work, the existence of the miscibility gap in a phase described with a substitutional solution model is analyzed for a binary system. When a miscibility gap exists in the phase, the second derivative of Gibbs energy $G(x)$ has two zero points in interval (0, 1). The quick and direct judgment for the existence of the miscibility gap is established for the cases of $n = 0$ and $n = 1$, respectively. For $n \geq 2$, eigenvalue method is used to solve a corresponding polynomial system equivalent to $G''(x) = 0$. In particular, for a given L_0 as well as L_0 and L_1, we propose a numerical method to find the numerical ranges for L_1 as well as L_2 in which there is a miscibility gap in the phase. A home-made code has been written to compute the Al-Zn and Al-In binary phase diagrams with the present algorithm.

Based on the chain rule of the derivative of compound function, we deduce the first and second derivatives of Gibbs energy with respect to composition for a phase described with a sublattice model in a binary system. The method to detect the miscibility gap in terms of interaction parameters can be generalized to a sublattice model in which the Gibbs energy has two internal variables. Moreover, in view of the derivatives, we have developed a system of equations to efficiently compute the Gibbs energy curve of a phase described with a sublattice model.

Acknowledgements

This work was supported by the National Key Research and Development Program of China (grant numbers 2017YFB0701700, 2017YFB0305601). Thank is also due to Prof. Bo Sundman for helpful discussion.

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EFIKASAN ALGORITAM ZA ODREĐIVANJE PREKIDA U RASTVORLJIVOSTI U BINARNOM SUPSTITUCIONOM RASTVORU

T. Fu[a], Y. Du [b,*], Z.-S. Zheng [a,*], Y.-B. Peng [c], B. Jin [b], Y.-L. Liu [b], C.-F. Du [a], S.-H. Liu [b], C.-Y. Shi [b], J. Wang [b]

[a*] Fakultet za matematiku i statistiku, Centralno južni univerzitet, Čangša, Hjunan, Kina
[b] Glavna državna laboratorija metalurgije praha, Centralno južni univerzitet, Čangša, Hjunan, Kina
[c] Fakultet za metalurgiju i inženjerstvo materijala, Univerzitet tehnologije u Hjunanu, Kina

Apstrakt

U postojećoj literaturi nema detaljnih opisa o tome kako analitički detektovati postojanje prekida u rastvorljivosti na osnovu interakcionih parametara. U ovom radu je predložen metod za određivanje verovatnoće postojanja prekida u rastvorljivosti u binarnom supstitucionom rastvoru, a uz pomoć interakcionih parametara. Raspon između poslednjeg interakcionog parametra i prethodnih parametara se analizira da bi se dobio skup doslednih parametara povezanih sa prekidom u rastvorljivosti. Osim toga, izračunati su prvi i drugi izvod Gibsove energije u odnosu na sastav faze opisane pomoću modela podrešetke u binarnom sistemu. Fazni dijagrami Al-Zn i Al-In su proračunati uz pomoć sopstvenog koda da bi se verifikovala efikasnost ovih tehnika. Metod za otkrivanje prekida u rastvorljivosti na bazi interakcionih parametara može se generalizovati i na modele podrešetki. Na kraju, razvijen je sistem jednačina da bi se efikasno izračunala kriva Gibsove energije kod faze opisane pomoću modela podrešetke.

Ključne reči: *Termodinamički proračuni; Proračuni ravnoteže; Fazni dijagram; Prekid u rastvorljivosti; Algoritam.*