
Free energy determination of a binary alloy around the equilibrium based on the order parameter

EL AZZOUZI Fatima^{*1} and EL KHOMSSI Mohammed¹

¹Department of Mathematics, Laboratory of Modeling and Scientific Calculation, Sidi Mohamed Ben Abdellah University, College of Science and Technology, BP 2202, Route d'Imouzzer, Fez, Morocco.

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Abstract

In this paper, we have determined the free energy of a binary alloy for any order and it is showed that the number of equilibrium states of the system is obtained by the Taylor expansion to the 4-th order choice. We explicitly determine the stable states of alloy which are characterized by the free energy.

Keywords: Binary alloy; Equilibrium states; Free energy; Taylor expansion.

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1 Introduction and motivation

a. Model to study

Let us consider a binary alloy constituted of a crystal structure¹ of N sites randomly occupied by N_A atoms of type A and N_B atoms of type B [1] (figure 1).

Let us take the following data that characterizes the model to study (figure 1):

T : the absolute temperature.

$C_X = \frac{N_X}{N}$: the X atom concentration.

ε_{XY} : the interaction between the species X and Y .

P_{XY} : the probability for which an atom of type X has a neighbor of type Y .

z : the number of neighbors of each atom of type X or Y .

k_B : the Boltzmann constant.

S : the system entropy.

U : the internal energy of the system.

^{*}Corresponding author: E-mail: fati.elazzouzi@gmail.com

¹In mineralogy and crystallography, a crystal structure is a unique arrangement of atoms in a crystal. A crystal structure is composed of a unit cell, a set of atoms arranged in a particular way; which is periodically repeated in three dimensions on a lattice [2].

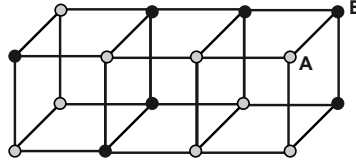


Figure 1: Binary alloy.

If we note Ω the space of the possible positions, then the number of permitted configurations is nothing but:

$$\text{card } \Omega = |\Omega| = \frac{N!}{N_A! N_B!}$$

Based on this formula and the Stirling's approximation [1][3][4], we obtain the expression (1.1) of the Boltzmann's microscopic entropy based on the concentration:

$$\frac{S}{N} = S_0 - k_B(c_A \ln c_A + c_B \ln c_B) \quad \text{with} \quad S_0 = k_B \ln N \quad (1.1)$$

b. Free energy formula

For the ideal case, that is to say the atoms of a different species are in very weak interaction or identical, the thing which be translated by:

$$\varepsilon_{AB} = \varepsilon_{AA} = \varepsilon_{BB}$$

This situation provides to suppose that the internal energy $U = U_0$ is independent of the atoms arrangement in sites. Thus, giving a reminder that the free energy formula is $F = U - TS$, the free energy of the ideal solution is obtained by the following formula [1][5]:

$$E_{id} = \frac{F_{id}}{N} = \frac{U_0}{N} - TS_{id} = \frac{U_0}{N} - T \frac{S}{N} = E_0 + k_B T (c_A \ln c_A + c_B \ln c_B) \quad (1.2)$$

With $E_0 = \frac{U_0}{N} - k_B T \ln N$. In the regular case, the entropy always result from the randomly acquisition of sites: the regular entropy notated by S_{reg} is equal to S_{id} , that is to say $S_{reg} = S_{id}$. Whereas, the internal energy considers the interactions of neighboring species. The probability laws of atoms can be written, for the equiprobability and the symmetry reasons, as:

$$\begin{cases} P_{AB} + P_{AA} = P_{BA} + P_{BB} \\ c_A P_{AB} = c_B P_{BA} \end{cases} \quad (1.3)$$

The symmetry, equiprobability as well as the interactions between the A and B species provide to write the regular internal energy, which is notated by U_{reg} , as [1][5]:

$$U_{reg} = \frac{1}{2} N c_A z (P_{AB} \varepsilon_{AB} + P_{AA} \varepsilon_{AA}) + \frac{1}{2} N c_B z (P_{BA} \varepsilon_{BA} + P_{BB} \varepsilon_{BB}) \quad (1.4)$$

The $\frac{1}{2}$ factor is used to not count the liaisons twice. The relation (1.3) and the fact that $c_A + c_B = 1$ provide, if we pose $\varepsilon = \varepsilon_{AB} - \frac{1}{2} (\varepsilon_{AA} + \varepsilon_{BB})$, to obtain the following expression:

$$U_{reg} = U_0 + N z c_A \varepsilon P_{AB} \quad (1.5)$$

With a reasonable hypothesis which consists to do the approximations of the average field by their average values which provide to confuse P_{AB} with c_B , the formulas overview of the regular internal energy and the entropy give us the free energy of the regular solution:

$$E_{reg} = E_0 + z c_A c_B \varepsilon + k_B T (c_A \ln c_A + c_B \ln c_B) \quad (1.6)$$

Consequently, we are interested in this free energy of the regular solution since the one of the ideal solution is a particular case. Indeed, it is enough to take $\varepsilon = 0$. Thereafter, to make our paper easy to read, we use the following notation: $E_{reg} = E$.

2 Free energy around the equilibrium

a. Free energy formula based on the order parameter

Our purpose is to write E based on a parameter which is linked to atoms concentration. For that, we are going to exploit the symmetry compared to $\frac{1}{2}$. Indeed, our function is the sum, to within a constant, of two symmetric functions in relation to $\frac{1}{2}$, the term $zc_A c_B = z\varepsilon(c_A - c_A^2)$ with $c_B = 1 - c_A$, and its derivative is worth $z\varepsilon(1 - 2c_A)$, the other term has $k_B T \ln\left(\frac{c_A}{1-c_A}\right)$ as derivative. Both of derivatives cancel each other out in $c_A = \frac{1}{2}$. In addition, it is about two even functions in relation to this axis. We notice that $E(1 - c_A) = E(c_A)$. Let us consider:

$$\eta \in \left] -\frac{1}{2}, \frac{1}{2} \right[$$

Such as $c_A = \frac{1}{2} - \eta$, it is evident that $c_B = \frac{1}{2} + \eta$. Based on this new parameter, called order parameter, η the free energy for an atom can be written as:

$$E(\eta) = E_0 + z \left(\frac{1}{4} - \eta^2 \right) \varepsilon + k_B T \left[\frac{1}{2} \ln \left(\frac{1}{4} - \eta^2 \right) + \eta \ln \left(\frac{\frac{1}{2} + \eta}{\frac{1}{2} - \eta} \right) \right] \quad (2.1)$$

For the physicists, it is interesting to study the variation of this energy, **because** the equilibrium is characterized by its minimum. After simplification of calculation, we have:

$$\frac{dE(\eta)}{d\eta} = -2z\varepsilon\eta + k_B T \ln \left(\frac{\frac{1}{2} + \eta}{\frac{1}{2} - \eta} \right) \quad (2.2)$$

$$\frac{d^2 E(\eta)}{d\eta^2} = 2 \left(\frac{2k_B T}{1 - 4\eta^2} - z\varepsilon \right) \quad (2.3)$$

The critical temperature is obtained when we have a perfect order, that is to say $c_A = c_B = \frac{1}{2}$ where $\eta = 0$. The second derivative of the free energy can be canceled $\frac{d^2 E(\eta)}{d\eta^2} = 0$ when $\eta = 0$ which implies that:

$$T = T_c = \frac{z\varepsilon}{2k_B} \quad (2.4)$$

b. Justification of order word

It is good to notice that the justification of the order word come from the sign of ε , itself is in relation to η . Indeed, if $\varepsilon > 0$ the free energy of the mixture is higher than that one of phases, this corresponds to a segregation tendency, the nature of the structure is in order. On the other hand, if $\varepsilon < 0$ the structure has a tendency to mixture that is to say a disorder. The analysis of this free energy uses a polynomial approximation, it is the aim of the following section.

3 Polynomial approximation and critical points

3.1 Approximation

The η variable play a role of order parameter. In the physical works and articles, even the Taylor expansion of free energy is given to 2 or 4-th order, and in accordance with the polynomial canonical

basis $(1, x, x^2, \dots, x^n)$. In this work we propose the Taylor expansion to any order, hence the following result [1][6][7][8]:

Lemma 3.1. *The free energy to the n – th order is approximated by:*

$$E(\eta) = E_1 + 2k_B(T - T_c)\eta^2 + \frac{4}{3}k_BT\eta^4 + k_BT \sum_{k=3}^n \frac{(2\eta)^{2k}}{2k(2k-1)} + O(\eta^{2n+1}). \quad (3.1)$$

With $E_1 = E_0 + \frac{z\varepsilon}{4} + k_BT \ln 2 = \frac{U_0}{N} + \frac{k_BT}{2} (T_c - 2 \ln(\frac{N}{2}) \cdot T)$.

Proof. Since the intervening functions in the energy given in (2.1) are $C-n$ functions in their definition field compared to η , the asymptotic expansion of the different terms to the n – th order are:

$$\begin{aligned} \frac{1}{2} \ln \left(\frac{1}{4} - \eta^2 \right) &= -\ln 2 - \frac{1}{2} \left(4\eta^2 + \frac{(2\eta)^4}{4} + \frac{(2\eta)^6}{6} + \dots + \frac{(2\eta)^{2n}}{2n} + O(\eta^{2n}) \right) \\ \eta \ln \left(\frac{1}{2} + \eta \right) &= -\eta \ln 2 + \eta \left(2\eta - \frac{(2\eta)^2}{2} + \frac{(2\eta)^3}{3} - \dots + (-1)^{n-1} \frac{(2\eta)^n}{n} + O(\eta^n) \right) \\ -\eta \ln \left(\frac{1}{2} + \eta \right) &= \eta \ln 2 + \eta \left(2\eta + \frac{(2\eta)^2}{2} + \frac{(2\eta)^3}{3} + \dots + \frac{(2\eta)^n}{n} + O(\eta^n) \right) \end{aligned}$$

By replacing each term by its equivalent expression, we obtain:

$$E(\eta) = E_0 + z\varepsilon \left(\frac{1}{4} - \eta^2 \right) - k_BT \ln 2 + 2k_BT\eta^2 + \frac{4}{3}k_BT\eta^4 + k_BT \sum_{k=2}^n \frac{(2\eta)^{2k}}{2k(2k-1)} + O(\eta^{2n+1}), \quad k \in \mathbb{N}. \quad (3.2)$$

Let us put $F_0 = E_1$, $F_1 = 2k_B(T - T_c)$, $F_2 = \frac{4}{3}k_BT$ and $F_k = \frac{k_BT}{2k(2k-1)} \quad \forall k \geq 3$.

The polynomial that gives the approximation to the n – th order of the free energy can be written as:

$$E(\eta) = F_0 + F_1\eta^2 + F_2\eta^4 + P(\eta) + O(\eta^{2n+1}) \quad (3.3)$$

With $P(\eta) = \sum_{k=3}^n F_k \cdot (2\eta)^{2k} \geq 0 \quad \forall \eta$. Hence, the lemma result. \square

3.2 Critical points and equilibrium states

a. Decomposition of the free energy writing

Lemma 3.2. *The E free energy to the 4 – th order based on η parameter can be written by:*

$$E(\eta) = F_0 + F_1\eta^2 + F_2\eta^4 + O(\eta^4) \quad (3.4)$$

It is enough to take $O(\eta^4) = P(\eta) = \sum_{k=3}^{n-1} F_k \cdot (2\eta)^{2k-4}$.

We notice that the free energy to the n – th order can be written as a sum of two polynomials.

$$E(\eta) = E_4(\eta) + P_3(\eta) + O(\eta^{2n+1}) \quad (3.5)$$

Where $E_4(\eta) = F_0 + F_1\eta^2 + F_2\eta^4$ and $P_3(\eta) = \sum_{k=3}^n F_k \cdot (2\eta)^{2k}$.

b. Justification of the 4 – th order choice

Theorem 3.3. For all n order,

$$\min E(\eta) = \min E_4(\eta) \quad (3.6)$$

Proof. It exists a such that $0 < a < \frac{1}{2}$, the free energy E is strictly increasing around $\left] -\frac{1}{2}, -a \right[$ and $\left] a, \frac{1}{2} \right[$. Therefore, there are not any minimum of the free energy E in $\left] -\frac{1}{2}, -a \right[\cup \left] a, \frac{1}{2} \right[$. The question of minimal energy comes up only in $I = [-a, a] \subset \left] -\frac{1}{2}, \frac{1}{2} \right[$.

E_4 and P are two continuous functions on I . Since $E_4(\eta) \geq \min E_4(\eta)$ and $P(\eta) \geq \min P(\eta)$ for all $\eta \in I$, so:

$$\min (E_4(\eta) + P(\eta)) \geq \min E_4(\eta) + \min P(\eta) \quad (3.7)$$

Let us suppose by absurd that:

$$\min (E_4(\eta) + P(\eta)) > \min E_4(\eta) + \min P(\eta)$$

And let η_0 be the point that realizes the minimum. Since I is compact and E_4 and P are continuous, therefore the minimum in η_0 is attended. Let η_n a sequence that converges to η_0 , then $E_4(\eta_n) + P(\eta_n) = (E_4 + P)(\eta_n)$. By passage to limit:

$$\begin{aligned} \lim_{\eta_n \rightarrow \eta_0} [E_4(\eta_n) + P(\eta_n)] &= E_4(\lim \eta_n) + P(\lim \eta_n) \\ &= E_4(\eta_0) + P(\eta_0) \\ &= (E_4 + P)(\eta_0) \end{aligned}$$

Absurd. So:

$$\min (E_4(\eta) + P(\eta)) \leq \min E_4(\eta) + \min P(\eta) \quad (3.8)$$

By (3.7) and (3.8) we have:

$$\min (E_4(\eta) + P(\eta)) = \min E_4(\eta) + \min P(\eta) \quad (3.9)$$

Well, $P(\eta) = \sum_{k=3}^n F_k \cdot (2\eta)^{2k}$ then,

$$P'(\eta) = \sum_{k=3}^n 4k F_k \cdot (2\eta)^{(2k-1)}$$

Since $4k F_k > 0 \forall k$, so $P'(\eta) = 0 \iff \eta = 0$. Thus, the unique critical point of P is $(0, 0)$.

$$P''(\eta) = \sum_{k=3}^n 8k(2k-1) F_k \cdot (2\eta)^{(2k-2)}$$

Since $k(2k-1) F_k > 0 \forall k \geq 3$, then $P''(\eta) > 0 \forall \eta \in]0, \frac{1}{2}[$, therefore P is strictly convex and the unique minimum of P is 0. Hence,

$$\min E(\eta) = \min E_4(\eta)$$

Which explain the fact to do the analysis of a 4 – th order Taylor expansion. We conclude that the 4 – th order is necessary and sufficient for the stability study of the alloy. \square

After the justification of the 4 – th order choice, we are going to study the stability for $n = 4$.

c. Study for the $4 - th$ order case

Let us consider the free energy up to the $4 - th$ order, and let F_0 , F_1 and F_2 be the coefficients earlier defined. Since E is even, we do the analysis in $[0, \frac{1}{2}]$. Let us put,

$$T_c^* = \frac{2U_0}{Nk_B(2\ln(\frac{N}{2}) - 1)} \quad (3.10)$$

And,

$$T_c^{**} = \frac{U_0}{Nk_B \ln(\frac{N}{2})} + \frac{1}{2\ln(\frac{N}{2})} T_c \quad (3.11)$$

We have then:

Case where $T = T_c$, $T = T_c^*$ or $T = T_c^{}$**

1. In the case where $T = T_c^*$ we have $F_0 = F_1 = 0$. And $E_4(\eta)$ can be written as:

$$E_4(\eta) = \frac{8U_0}{3N(2\ln(\frac{N}{2}) - 1)} \eta^4 \quad (3.12)$$

In that case,

$$\min_{\eta} E_4 = E_4(0) = 0 \quad (3.13)$$

2. In the case where $T = T_c$, we have $F_1 = 0$. Consequently $E_4(\eta)$ can be written as:

$$E_4(\eta) = F_0 + F_1 \eta^4 \quad (3.14)$$

And,

$$\min E_4 = E_4(0) = F_0 = \frac{U_0}{N} + \left(\frac{1}{2} - \ln(\frac{N}{2})\right) k_B T_c \quad (3.15)$$

- If $T_c < T_c^*$, then $F_0 > 0$, therefore $E_4(\eta) > 0$ and it admits a unique value $\eta = 0$ that realizes the minimal state, consequently:

$$\min_{\eta} E_4 = E_4(0) = F_0 \quad (3.16)$$

- And if $T_c > T_c^*$ then $F_0 < 0$. Let be $\frac{dE_4(\eta)}{d\eta} = 4F_2\eta^3$, $E_4(\eta)$ admits a unique root, and:

$$\min_{\eta} E_4 = E_4(0) = F_0 \quad (3.17)$$

3. In the case where $T = T_c^{**}$, then $F_0 = 0$. The free energy can be written as then:

$$E_4(\eta) = F_1 \eta^2 + F_2 \eta^4 \quad (3.18)$$

And,

$$\frac{dE_4(\eta)}{d\eta} = 2\eta(F_1 + 2F_2\eta^2) \quad (3.19)$$

- If $T_c < T_c^*$, then $F_1 > 0$. Consequently, $E_4(\eta)$ admits a unique root $\eta = 0$ that realizes the minimum, then:

$$\min_{\eta} E_4 = E_4(0) = 0 \quad (3.20)$$

- If $T_c > T_c^*$, then $F_1 < 0$:

$$\min_{\eta} E_4 = E_4\left(\sqrt{\frac{-F_1}{2F_2}}\right) = \frac{-F_1^2}{4F_2} \quad (3.21)$$

Case where $T \neq T_c$, $T \neq T_c^*$ or $T \neq T_c^{}$**

In this case, the free energy can be written as the following form:

$$E_4(\eta) = F_0 + F_1\eta^2 + F_2\eta^4 \quad (3.22)$$

And,

$$E_4'(\eta) = 2\eta (F_1 + 2F_2\eta^2) \quad (3.23)$$

1. If $T > T_c^{**}$, then $F_0 > 0$, so we have two possible cases:

- If $T_c < T_c^*$, then $F_1 > 0$. Therefore,

$$\min E_4(\eta) = E_4(0) = F_0 = \frac{U_0}{N} + \frac{k_B}{2} (T_c - 2 \ln(\frac{N}{2})T) \quad (3.24)$$

- On the other hand, if $T_c > T_c^*$, then $F_1 < 0$. We distinguish two possibilities then:

- If $F_0 < \frac{F_1^2}{4F_2}$:

$$\min_{\eta} E_4 = E_4 \left(\sqrt{\frac{-F_1}{2F_2}} \right) = F_0 - \frac{F_1^2}{4F_2} < 0 \quad (3.25)$$

- if $F_0 > \frac{F_1^2}{4F_2}$,

$$\min_{\eta} E_4 = E_4 \left(\sqrt{\frac{-F_1}{2F_2}} \right) = F_0 - \frac{F_1^2}{4F_2} > 0 \quad (3.26)$$

2. If $T < T_c^{**}$, then $F_0 < 0$, we distinguish:

- If $T_c < T_c^*$, then $F_1 > 0$. So, $E_4(\eta)$ admits a unique root and $(0, F_0)$ as an equilibrium point:

$$\min_{\eta} E_4 = E_4(0) = F_0 \quad (3.27)$$

- However, if $T_c > T_c^*$, then:

$$\min_{\eta} E_4 = E_4 \left(\sqrt{\frac{-F_1}{2F_2}} \right) = F_0 - \frac{F_1^2}{4F_2} < 0 \quad (3.28)$$

3.3 Summary table: Equilibrium Values

It is evident that the signs of the coefficients F_0 and F_1 play a fundamental role to determine the stability of the system, that is to say the minimum of E . As we have previously seen:

$$\min_{\eta} E = \min_{\eta} E_4$$

We summarize all of possible situations of the free energy in the summary table (Table 1).

3.4 Possible curves of free energy

We represent all the possible situations of free energy in the following graphs:

Table 1: Summary table

	F_0	F_1	Thermal field	$\min_{\eta} E$
case 1	0	0	$T = T_c^*$	0
case 2	+	0	$T = T_c$ and $T_c < T_c^*$	$\frac{U_0}{N} + \left(\frac{1}{2} - \ln\left(\frac{N}{2}\right)\right) k_B T_c$
case 3	-	0	$T = T_c$ and $T_c > T_c^*$	$\frac{U_0}{N} + \left(\frac{1}{2} - \ln\left(\frac{N}{2}\right)\right) k_B T_c$
case 4	0	+	$T = T_c^{**}$ and $T_c < T_c^*$	0
case 5	0	-	$T = T_c^{**}$ and $T_c > T_c^*$	$-\frac{3}{4} k_B \frac{(T - T_c)^2}{T}$
case 6	+	+	$T > T_c^{**}$ and $T_c < T_c^*$	$\frac{U_0}{N} + \frac{k_B}{2} (T_c - 2 \ln\left(\frac{N}{2}\right) T)$
case 7	+	-	$T > T_c^{**}$, $T_c > T_c^*$ and $F_0 < \frac{F_1^2}{4F_2}$	$\frac{U_0}{N} + k_B \left[\left(2 - \frac{3T_c}{4T}\right) T_c - \left(\ln\left(\frac{N}{2}\right) + \frac{3}{4}\right) T \right]$
case 8	+	-	$T > T_c^{**}$, $T_c > T_c^*$ and $F_0 > \frac{F_1^2}{4F_2}$	$\frac{U_0}{N} + k_B \left[\left(2 - \frac{3T_c}{4T}\right) T_c - \left(\ln\left(\frac{N}{2}\right) + \frac{3}{4}\right) T \right]$
case 9	-	+	$T < T_c^{**}$ and $T_c > T_c^*$	$\frac{U_0}{N} + \frac{k_B}{2} (T_c - 2 \ln\left(\frac{N}{2}\right) T)$
case 10	-	-	$T < T_c^{**}$ and $T_c > T_c^*$	$\frac{U_0}{N} + k_B \left[\left(2 - \frac{3T_c}{4T}\right) T_c - \left(\ln\left(\frac{N}{2}\right) + \frac{3}{4}\right) T \right]$

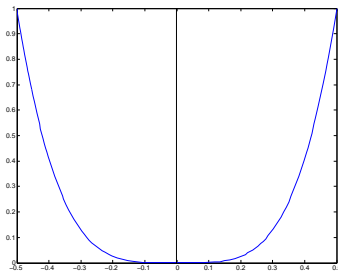


Figure 2: $F_0 = F_1 = 0$

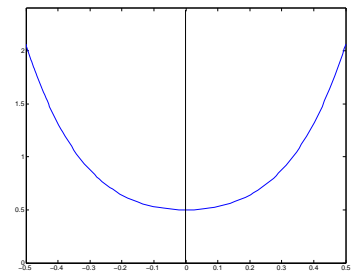


Figure 3: $F_1 > 0; F_0 > 0$

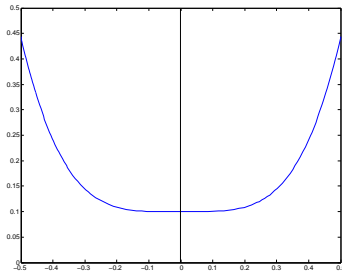


Figure 4: $F_1 = 0; F_0 > 0$

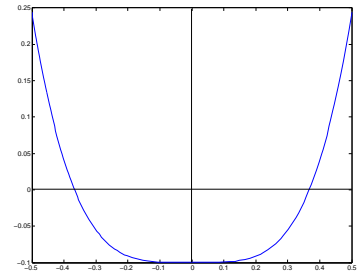


Figure 5: $F_1 = 0; F_0 < 0$

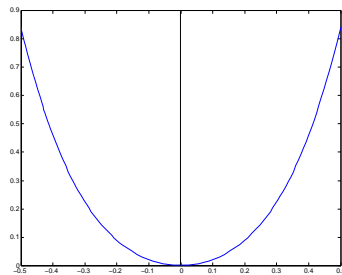


Figure 6: $F_0 = 0; F_1 > 0$

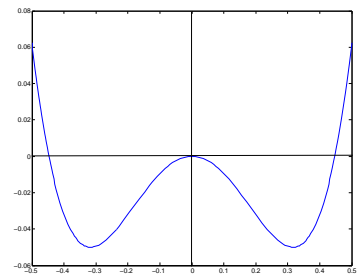


Figure 7: $F_0 = 0; F_1 < 0$

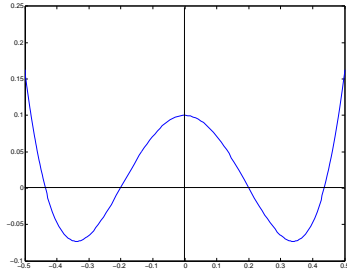


Figure 8: $F_0 > 0; F_1 < 0$
et $F_0 < \frac{F_1^2}{4F_0}$

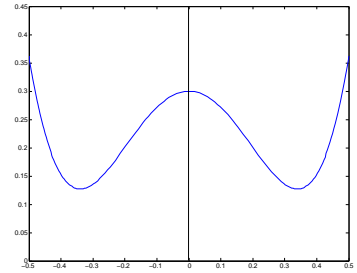


Figure 9: $F_0 > 0; F_1 < 0$
et $F_0 > \frac{F_1^2}{4F_0}$

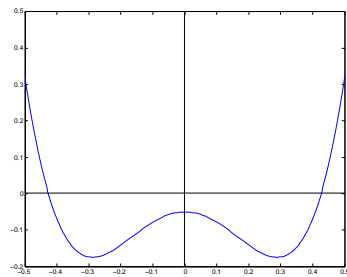


Figure 10: $F_0 < 0; F_1 < 0$

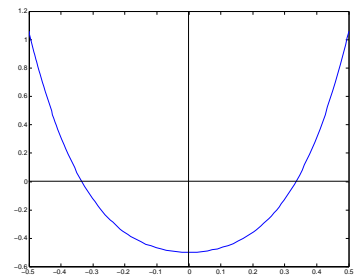


Figure 11: $F_0 < 0; F_1 > 0$

Remark 3.1. fundamental

1. We have proposed a logical procedure to do analysis of free energy which characterizes the stability of a binary alloy. Indeed, the value of the temperature field in relation to critical values of T_c , T_c^* and T_c^{**} provide to determine the F_0 and F_1 signs, nay their values, which have facilitated to us to analyze the minimum matter of free energy linked to the stability of system.
2. The terms of minimal free energy are always characterizes by U_0 , T_c and N .

4 Conclusions

In this article, we have obtained two results:

1. The first translates into the fact to show that the 4 – *th* order Taylor expansion is necessary and sufficient to approximate the free energy of a binary alloy.
2. Finally, based on the continuity we have determined the minimal states that characterize the system stability.

Acknowledgment

A brief acknowledgement section may be given after the conclusion section just before the references. The acknowledgments of people who provided assistance in manuscript preparation, funding for research, etc. should be listed in this section.

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