

ON THE FREE ENERGETICS OF BINARY METALLIC SOLID SOLUTIONS

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Introduction

A homogeneous solid solution supercooled inside the miscibility gap will evolve toward its new equilibrium state. This may be accomplished in two ways, either by fluctuations infinitesimally small in amplitude but extended in space or by fluctuations that are intense and localized, as stated by Gibbs (1). As long as the system becomes non uniform, transport phenomena will be produced by the gradient in the intensive parameters defining the system. In the thermodynamics of irreversible processes linear laws are supposed to be valid (e.g. Fick's laws for diffusion) between the fluxes and all the generalized thermodynamic forces. Non-uniform concentration introduces an excess free energy called the gradient energy (2)

$$F = \int [f + K (\nabla C)^2 + \dots]$$

so that the thermodynamic force is created by the change δF in the free energy due to a local change δC in the concentration. For closed system, at constant temperature and volume, this force vanishes for the non-uniform concentration distributions for which free energy is stationary. The resulting states are relatively stable states, although a metastable or an unstable state can also be obtained.

II. Configurational free energy and gradient coefficient

We consider a f.c.c. binary solid solution of the $L1_0$ type (CuAu). In order to take correctly into account interactions between nearest neighbour atoms (specially the characteristic feature of the f.c.c. structure that there are nearest neighbour atoms among the nearest neighbours of any site) we use the quasi chemical tetrahedron approximation developed by Yang and Li (3). This is the simpler analytically tractable approximation which predicts the right first kind order-disorder transition for this structure (4). To simplify the statement we consider here a one dimensional concentration along one of the crystallographic axes ([100]). A concentration parameter defined plane permits to calculate the free energy from a purely statistical

point of view, in the rigid atom assumption.

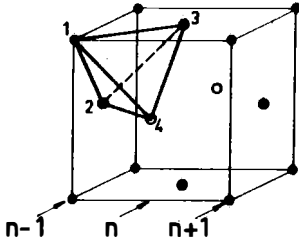


FIG.1.

The tetrahedron approximation for the f.c.c. structure.

We shall specify the occupation of a site i situated in the n^{th} plane by $q_{i,n}$: $q_{i,n} = 1$ if this site is occupied by a A atom,
 $= 0$ if it is occupied by a B atom.

Then the f.c.c. structure is divided in four interpenetrating simple cubic lattices, and the interactions decomposed in tetrahedrons, each of them having a corner on each of the sublattices (fig. 1).

Let N_1 be the number of sites by plane.

The intermediate variables will be the number $N_1 [q_{1,n}, q_{2,n}, q_{3,n+1}, q_{4,n+1}]$ of tetrahedrons having the configuration $q_{1,n}, q_{2,n}, q_{3,n+1}, q_{4,n+1}$, for all n . They are obtained by the standard quasi-chemical approximation with

$$\sum_i [q_{1,n}, q_{2,n}, q_{3,n+1}, q_{4,n+1}] = 1 \quad (1)$$

$$\sum_i q_{i,n} [q_{1,n}, q_{2,n}, q_{3,n+1}, q_{4,n+1}] = C_n \quad i = 1, 2 \quad (2)$$

$$\sum_i q_{i,n+1} [q_{1,n}, q_{2,n}, q_{3,n+1}, q_{4,n+1}] = C_{n+1} \quad i = 3, 4 \quad (3)$$

Detailed calculations are not given here and will be published elsewhere

(5) ; the final result is :

$$F = - N_1 k_B T \sum_n \left\{ \ln \phi_{n,n+1} + 3 [C_n \ln C_n + (1 - C_n) \ln (1 - C_n)] - 2 [C_n \ln \mu_n + C_{n+1} \ln \mu'_{n+1}] \right\} \quad (4)$$

$$\text{where } \phi_{n,n+1} = X^3 + 2 (\mu_n + \mu'_{n+1}) X^{3/2} + (\mu_n^2 + \mu'_{n+1}{}^2 + 4 \mu_n \mu'_{n+1}) X + 2 \mu_n \mu'_{n+1} (\mu_n + \mu'_{n+1}) X^{3/2} + \mu_n^2 \mu'_{n+1}{}^2 X^3 \quad (4 a)$$

and $X = \exp \left(- \frac{2v}{k_B T} \right)$, $v = \frac{1}{2} (v_{AA} + v_{BB}) - v_{AB}$ being the interaction energy between nearest neighbours.

The μ_n and μ'_{n+1} are Lagrange multipliers introduced by relations (2) and (3), and will be determined by :

$$\mu_n \frac{\partial \ln \phi_{n,n+1}}{\partial \mu_n} = 2 C_n \quad \text{and} \quad \mu'_{n+1} \frac{\partial \ln \phi_{n,n+1}}{\partial \mu'_{n+1}} = 2 C_{n+1} \quad (5)$$

In the case where the concentration is slowly varying from plane to plane, C_n may be considered as a continuous function of the position, and C_n is developed around $v = n + \frac{1}{2}$

$$C_n = C_v - \frac{1}{2} C'_v + 1/8 C''_v \quad \text{with} \quad C'_v = \frac{dC}{dv}, \quad C''_v = \frac{d^2C}{dv^2}$$

Higher order terms in the development are neglected for small gradients and we obtain the usual form of Landau - Lifshitz (2) and Cahn-Hilliard(6) expression for the inhomogeneous system in the 'continuum' approximation

$$F = N_1 \int [f(C_n) + K(C_n) (\nabla C_n)^2 + \dots] dn \quad (6)$$

where $f(C_n)$ is the configurational free energy per atom of the uniform system of concentration C_n (fig.2):

$$f(C_n) = - k_B T \left[\ln \phi_n + 3 (C_n \ln C_n + (1-C_n) \ln (1-C_n)) - 4 C_n \ln \mu_n \right] + 6 (v_{AB} + (C_n - \frac{1}{2})(v_{AA} - v_{BB})) \quad (7)$$

where μ_n is the solution of eq. 5. with $C_n = C_{n+1}$, i.e. $\mu_n = \mu'_{n+1}$ and ϕ_n the corresponding expression from (4a).

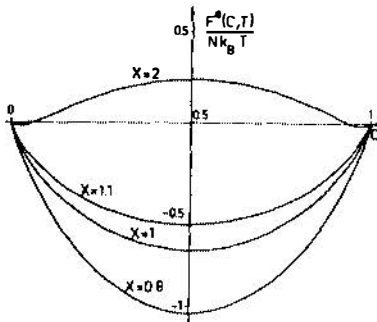


FIG.2.
Free energy of mixing per atom $F = f - 6 \{ C v_{AA} + (1-C) v_{BB} \}$ vs. composition.

The gradient coefficient K equals

$$K(C_n) = \frac{k_B T}{2} \frac{\phi_n}{\mu_n} \left[\left(X^{3/2} + 2 \mu_n X + \mu_n^2 X^{3/2} \right)^{-1} + (4 (1 - C_n) X^3 \mu_n^3 + 3 (3-4 C_n) X^{3/2} \mu_n^2 + 6 (1-2 C_n) X \mu_n + (1-4 C_n) X^{3/2})^{-1} \right]$$

We thus have an analytic expression for the configurational part of the gradient coefficient K which is plotted as a function of concentration in fig.3. It is strongly dependent on C, this is in contrast to the result obtained by Hillert (7) using Bragg-Williams approximation, who found it to be concentration independent.

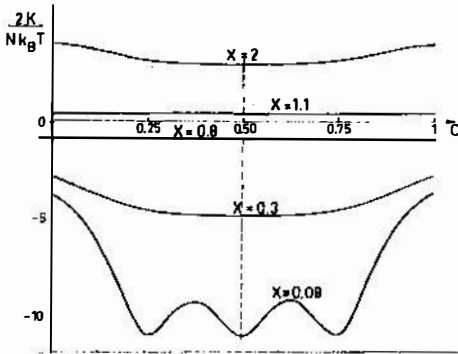


FIG.3.
The gradient coefficient K for
f.c.c. structure vs. composition.

When the interaction energy v is negative, i.e. $X > 1$, K is positive (i.e. positive departure from ideality with a miscibility gap). This is the case of spinodal decomposition considered by Hillert (7), Cahn (8) and others. When $v = 0$, the solution is ideal and there is no additional free energy for the inhomogeneous system.

The last case is $v > 0$, K becomes negative (i.e. negative departure from ideality), thus stabilizing large gradient represented by very short wavelength corresponding to ordered system (9). The continuum approximation becomes inappropriate, and we must return to the discrete set of equations .5., for all n . In this case, instead of using the discrete model it may be more useful to define an order parameter giving the concentration for two consecutive planes. Afterwards a continuum approximation may be used using order parameter instead of concentration parameter, as the variable to treat the case $v > 0$. This may be applicable to the slowly varying order parameter describing antiphase boundaries or long period superlattice in alloys (10).

III. Stationary states.

With the expression of free energy of the inhomogeneous system (eq.6) we can determine the stationary states. These are the states for which the total energy F is an extremum, taking into account the conservation of each species i.e. $\int (C_n - \bar{C}) dn = 0$. (8)

\bar{C} being the mean concentration of one component in the alloy.

This gives the Euler equation :

$$\frac{df}{dC_n} - \lambda - \frac{dK}{dC_n} C_n^2 - 2 K C_n^3 = 0 \quad (9)$$

λ being a constant to be calculated by eq.(8) : it is the generalized chemical potential for the non-uniform system.

We may integrate eq.(9) to obtain :

$$K(C_n) C_n'^2 = f(C_n) - \lambda(C_n - \bar{C}) - \text{Constant.} \quad (10)$$

To determine the nature of the solutions of this differential equation we shall use the generalized Poincaré theorem (11), based on the study of the nature of the singular points of the non-linear differential equation. For this purpose we rewrite equat. 9. by putting $v = C_n'$

$$\frac{dv}{dC_n} = \frac{\frac{df}{dC_n} - \lambda - \frac{dK}{dC_n} v^2}{2 v K(C_n)} \quad (11)$$

The singular points are defined by $\frac{df}{dC_n} - \lambda = 0$ and $v = 0$. Firstly, the positions of these singular points in the (v, C_n) space are independent of the gradient coefficient $K(C_n)$, and are function only of the uniform free energy curve $f(C_n)$.

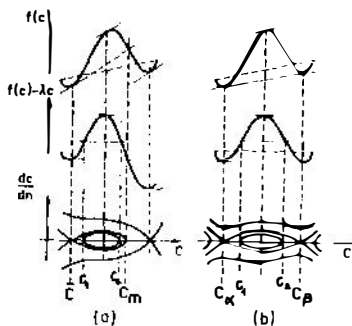


FIG.4.

The nature of the singular points for the variational problem from the free energy curve.

Looking at the nature of these singular points, we find that when $-\lambda_0 < \lambda < \lambda_0$ (λ_0 being the tangent at the inflexion points of $f(C_n)$), there are three singular points C_1, C_2, C_3 . Otherwise, there is only one, and the solutions C_n are unbounded, and thus of no physical interest. The type of the simple singularity (nodal, vortex or center, saddle, and spiral point) is determined by the sign of $D = 8 \frac{\partial^2 f}{\partial C^2} C_n - C_1 K(C_1)$. We shall confine ourselves to the case $v < 0$, i.e. $K > 0$. The points where $\frac{\partial^2 f}{\partial C^2} > 0$ are saddle points (fig.4) and those for which $\frac{\partial^2 f}{\partial C^2} < 0$, an additional test is necessary to differentiate between a center and a spiral point. Here, simply from equat. (10), it may easily be seen that the maximum number of points $v = 0$ for a given solution equals two so that the point may not be a spiral point, it is a center. The curve in the (v, C) space passing through the saddle point is called the separatrix and it corresponds to the critical nucleus, of maximum concentration C_m into a matrix of concentration \bar{C} . Closed curves, inside it, correspond to periodic distributions

of concentration oscillating between the two extreme values C_1 and C_2 there is a closed relation between the amplitude and the period of these states. Other states are unbounded and non physical.

In the special case where $\lambda = 6(v_{AA} - v_{BB})$ the two minima of $f(c)$ have the same value, and the separatrix passes through the two saddle points. The separatrix defines the state of equilibrium between two regions of concentration C_α and C_β . States inside the separatrix are still periodic states. All the states correspond to the mean concentration $\bar{C} = \frac{1}{2}$.

The position as well as the nature of the singular points are independent of the exact form of the gradient coefficient $K(C)$ and the nature of the stationary states are found identical as if K were supposed to be constant (12). Only the exact profile of the concentration for the stationary states is modified.

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DISCUSSION :

- H. Warlimont : Have you computed numerical results by using thermodynamic data of systems where they are sufficiently well known ?
- M. Avignon : No, not for the case of concentration fluctuations but we have done analogous calculation for order parameter as in the case of CuAuI (to be published) using the general ideas of inhomogeneous systems.
- J.L. Meijering : If the order parameter would go like a square wave instead of a sinusoidal wave, one could not understand the higher entropy of CuAuI (versus CuAuI), but the irrational period would surely be understandable.
- R. Roberge : In what respect do your study and predictions differ from the analysis of Cahn and Hilliard and the more recent work of Hilliard and co-workers ?
- M. Avignon : First of all, the use of Bragg-Williams approximation by Hilliard and co-workers is completely incorrect in case of F.C.C. systems. We have used the Yang-Lee method, which is the only correct way to treat the problem and our results are different from others. Also, we have studied the general instabilities of a metastable system, to give either a critical nucleus or a periodic variation of concentration or of the order parameter.