

METASTABILITY OF NON-UNIFORM SYSTEMS

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A simple theory is given, based on the nearest-neighbour regular solution model, that predicts that below a certain temperature non-uniform concentration profiles can be metastable in binary mixtures. The agreement with recently obtained experimental data is satisfactory.

1. Introduction

A theoretical treatment of non-uniform systems and its application to the spinodal decomposition of binary mixtures has been formulated by Cahn and co-workers [1–3]. In this treatment a non-uniform system reaches equilibrium via a diffusion process against the concentration gradient. In the final state the system consists of two homogeneous phases in which no concentration gradients are present. However, in a recent study in this laboratory Mesters et al. [4] found extensive concentration gradients of nickel in copper single crystals after thermal decomposition of $\text{Ni}(\text{CO})_4$ at the copper surface. An illustrative example of their results is presented in fig. 1. As expected on the basis of interfacial energy considerations, virtually no nickel is present at the copper surface, but its concentration rises steeply inside the crystal and extends over roughly 1000 atomic layers. This profile was found to be stable up to about 400°C although the profile flattened with increasing temperature.

In this letter we put forward a simple theoretical explanation for the observed effects based on the nearest-neighbour regular solution model (Bragg Williams or mean field approximation [5,6]). It is shown that below a certain temperature a concentration profile of the form found experimentally is in fact metastable.

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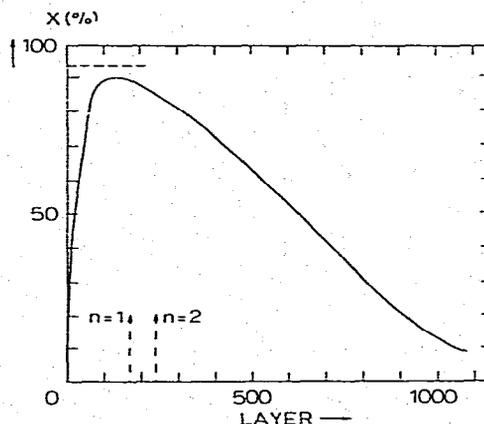


Fig. 1. Nickel fraction as a function of layer number for the Cu(110) surface following thermal decomposition of $\text{Ni}(\text{CO})_4$. After ref. [4].

2. Theory

The free energy per unit volume of mixing of N_A atoms A and N_B atoms B in the nearest-neighbour regular solution model is given by

$$f = \rho \{ \gamma \Omega x(1-x) + k_B T [x \ln x + (1-x) \ln(1-x)] \} . \quad (1)$$

Here ρ is the number of atoms per unit volume, x the mole fraction of atoms B, γ the number of nearest neighbours and Ω the weighted difference of the A–

A, B-B and A-B bond strengths,

$$\Omega = V_{AB} - \frac{1}{2}(V_{AA} + V_{BB}). \quad (2)$$

Assuming a non-uniform concentration profile of the form

$$x(z) = Ay e^{-z/\xi} \quad (3)$$

with ξ much larger than the distance d between the layers one finds for the free energy of mixing per unit area of surface:

$$\begin{aligned} F/k_B T &= (1/k_B T) \int_0^\infty f[x(z)] dz \\ &= \rho A \xi^2 \left[\frac{\gamma \Omega}{k_B T} \left(1 - \frac{1}{4}y\right) + \ln y \right. \\ &\quad \left. + \sum_{k=1}^\infty \frac{(k-1)!}{(k+1)^{k+2}} y^k - C - 2 \right], \quad (4) \end{aligned}$$

where $C = 0.577125\dots$ is Euler's constant and $y = A\xi$.

Here the Cahn-Hilliard gradient term $K(dx/dz)^2$, with $K \approx \gamma\Omega d^2$ has been neglected. This is justified for the non-uniformity in the concentration we are considering here, since it has a length scale $\xi \gg d$ and thus the contribution of the gradient term is $\gamma\Omega(d/\xi)^2 \ll \gamma\Omega$.

The concentration profile (3) has a maximum

$$x_{\max} = A\xi/e = y/e \quad (5)$$

at

$$z_{\max} = \xi. \quad (6)$$

Since physically $x \leq 1$ it follows from eq. (5) that $y \leq e$. The total number of penetrated nickel atoms per unit area is given by

$$\Gamma = \rho \int_0^\infty x(z) dz = \rho A \xi^2. \quad (7)$$

From eqs. (4) and (7) it is clear that the mixing free energy is proportional to the amount of nickel dissolved and further depends on the form of the non-uniform concentration profile only through the parameter y . Extrema of F for a fixed amount of dissolved amount nickel are found from

$$\frac{1}{4} \gamma \Omega / k_B T = \sum_{k=0}^\infty [k! / (k+1)^{k+2}] y^{k-1}. \quad (8)$$

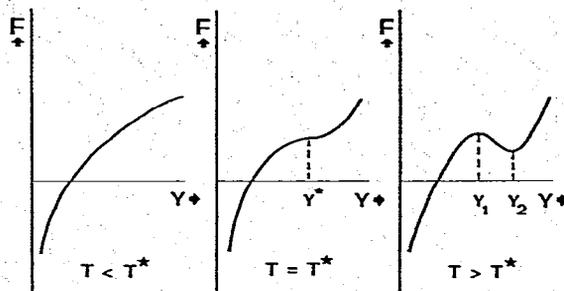


Fig. 2. Schematic representation of the behaviour of the free energy (F) as a function of the profile parameters $y = A\xi$, for $T < T^*$ (left-hand figure), $T = T^*$ (middle figure) and $T > T^*$ (right-hand figure).

Numerically we find from eq. (8):

(a) $k_B T / \gamma \Omega > 0.354$; F has no extrema.

(b) $k_B T / \gamma \Omega = k_B T^* / \gamma \Omega = 0.354$; F has an inflection point for $y = y^* = 2.29$. This corresponds to a distribution with a maximum $x_{\max} = y^*/e = 0.842$ at $z_{\max} = \Gamma / \rho y^* = 0.44 \Gamma / \rho$.

(c) $k_B T / \gamma \Omega < 0.354$; F has a maximum for $y_1 < y^*$ and a minimum for $y_2 > y^*$.

The behaviour of F is illustrated schematically in fig. 2. Note that the lowest value of F is reached for $y \rightarrow 0$, which corresponds to the limit of an uniform distribution. From the results above it appears that for temperatures $T < T^*$ (which in turn lies below the critical demixing temperature, $k_B T_c / \gamma \Omega = \frac{1}{2}$) a non-uniform distribution is metastable.

In order to check to what extent this conclusion depends on the chosen form of the concentration profile we repeated the above calculations for profiles of the form

$$x(z) = Az^n e^{-z/\xi}, \quad n = 2, 3, \dots \quad (9)$$

The free energy is then given by

$$\begin{aligned} \frac{F}{k_B T} &= \Gamma \left[\frac{\gamma \Omega}{k_B T} \left(1 - y \frac{(2n)!}{n! 2^{2n+1}}\right) \right. \\ &\quad \left. + \sum_{k=1}^\infty \frac{[n(k+1)!]}{n! k(k+1)^{k+n+2}} y^k + \ln y \right. \\ &\quad \left. + n \left(1 + \frac{1}{2} + \frac{1}{3} + \dots + 1/n - C\right) - n - 2 \right], \quad (10) \end{aligned}$$

where $y = A\xi^n$ and $\Gamma = \rho n! A \xi^{n+1}$. The free energy given by eq. (9) has qualitatively the same form as the previous expression. The extrema of F are now found from

$$\frac{\gamma\Omega}{k_B T} \frac{(2n)!}{n! 2^{2n+1}} = \sum_{k=0}^{\infty} \frac{[n(k+1)]!}{n!(k+1)^{kn+n+2}} y^{k-1} \quad (11)$$

For $n = 2$ one finds $k_B T^*/\gamma\Omega = 0.357$ for $y^* = 1.545$ corresponding to a distribution with a maximum $x_{\max} = 4y^*/e^2 = 0.839$ at $z_{\max} = \Gamma/\rho y^* = 0.65\Gamma/\rho$. Thus the value of the maximum is slightly lower and its position is somewhat further from the surface, but qualitatively the results are the same.

3. Discussion

As has been shown in section 2 a concentration profile of the form $Az \exp(-z/\xi)$ is metastable below a temperature T^* , equal to $0.354 \gamma\Omega/k_B$ (for $n = 1$) or $0.357 \gamma\Omega/k_B$ (for $n = 2$). The difference between the (local) minimum and the maximum value of F depends of course on $T^* - T$. For $T = 0.99 T^*$ one finds from eq. (8) for the profile $Az \exp(-z/\xi)$ that the maximum is located at $y_1 = 2.12$ and the minimum at $y_2 = 2.43$. The concentration profiles for these two cases are shown in fig. 3, for a total number

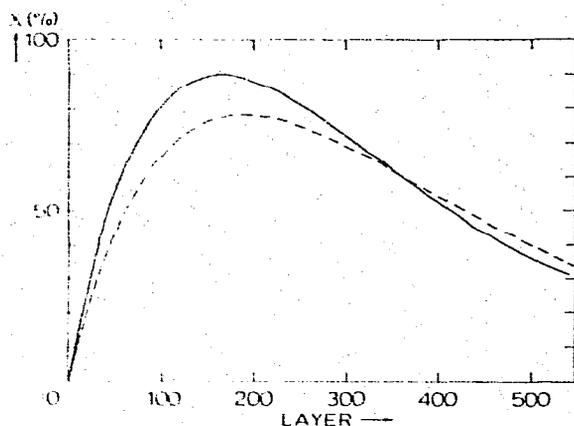


Fig. 3. Calculated concentration profiles corresponding to the local minimum (---) and the maximum (—) of the free energy. Parameters as described in text.

of penetrated nickel atoms of 400 per surface unit cell, which is roughly the experimental value deduced from fig. 1. The profiles are seen to be rather different. The difference in free energy per penetrated nickel atom in this case is from eq. (4) $F/\Gamma \approx 0.005 k_B T$. Taking into account that in order to change the profile at a surface unit cell a number of 400 atoms must participate collectively, one obtains an energy barrier of $2k_B T$ for this process. The stability of the non-uniform profile increases with increasing $T^* - T$ for example for $T = 0.95 T^*$ one finds an energy difference of $5k_B T$ per surface unit cell.

We now turn our attention to the experimental data displayed in fig. 1, taken at 200°C . In order to evaluate $k_B T/\gamma\Omega$ we use the mean field relation $k_B T/\gamma\Omega = 0.5$ with $T_c = 700 \text{ K}$ [7]. For $T = 200^\circ\text{C}$ one then obtains $k_B T/\gamma\Omega = 0.34$. For the profile with $n = 1$ this implies a maximum nickel fraction of 93% at layer 160. For the profile with $n = 2$ the corresponding values are 94% at layer 230. Both sets of values are indicated in fig. 1 and are seen to be qualitatively and even semi-quantitatively in agreement with the experimental data.

In summary we conclude that our approach predicts that non-uniform concentration profiles might be metastable below a certain temperature. The experimental results are well described by our theory.

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