КОМП'ЮТЕРНЕ МОДЕЛЮВАННЯ ТА МЕТОДИ ОБЧИСЛЕНЬ У ФІЗИЦІ ТА МАТЕМАТИЧНІЙ ФІЗИЦІ

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"ZERO STABILITY" OF THE TWO-PHASE SYSTEMS AND RANDOM WALK IN THE COMPOSITION SPACE.

The present paper considers possibilities of instability and random walk along the conode within two-phase region of composition space for binary or ternary alloy. Some simple models of such random walk are suggested.

Key words: diffusion, fluctuations, two-phase alloy, conode, random walk

I. Introduction

In this paper we are not presenting any new final results. Instead, we are trying to formulate some new problems.

To make things clear, let us start with "gedanken experiment" (so beloved by Einstein and his followers). Imagine diffusion couple consisting of two-phase alloy with composition 40% Sn+60%Pb (left) and another two-phase alloy 60%Sn+40%Pb (right). What will happen with coarsened concentration profile after long annealing of such couple at temperature lower than eutectic one for Sn-Pb solder (183^0C). Correct answer, according to classical thermodynamics, is "nothing will happen" [1, 2]. Indeed, both of two starting two-phase alloys are the mixtures (with different proportions) of the same two phases in equilibrium between them. It means that chemical potential of any component is the same in the grains of both phases:

$$\mu_A^\alpha = \mu_A^\beta, \mu_B^\alpha = \mu_B^\beta \qquad (1)$$

Thus, there is no gradient of chemical potentials (zero driving force) between starting members of diffusion couple. So, there will be no fluxes and no redistribution except effects related to capillary effects including coarsening.

Yet, this logic has one fundamental drawback – it does not take stochastic factor (fluctuations) into account. Fluctuations of fluxes and corresponding fluctuations of concentrations are inevitable in any real system due to two main reasons.

(1)   First reason of flux fluctuations is a so-called thermal noise (at atomic level) – it means local non-zero fluxes of all components even at equilibrium due to random nature of atomic migration. Typical spatial scale of such fluctuations in solid state is within few nanometers. In the stable phases (for example, stable solid solutions) the probability of fluctuation (as known from standard thermodynamics of fluctuations) is proportional to

$$exp\left(-N \frac{\frac{\partial^2 g}{\partial c^2}}{2kT} (C - \langle C \rangle)^2\right), \qquad (2)$$

(where N is a number of atoms in the region of fluctuation) so that mean squared concentration deviation

$$\sqrt{\langle (C - \langle C \rangle)^2 \rangle} = \sqrt{\frac{1}{N} \frac{kT}{\partial^2 g / \partial c^2}} \qquad (3)$$

In a two-phase region, formally speaking, Gibbs free energy per atom is a linear combination of its values for two phases in equilibrium (if one neglects the energy of interphase interfaces):

$$g = p^\alpha g^\alpha + p^\beta g^\beta, with\ C = p^\alpha C^\alpha + p^\beta C^\beta, \Delta C = \Delta p^\beta \cdot (C^\beta - C^\alpha). \qquad (4)$$

Thus,
$$\frac{\partial^2 g}{\partial c^2} = 0, \sqrt{< (C - < C >)^2 >} \to \infty \tag{5}$$

Physically it means **fixed equilibrium with respect to change of concentration or phase volume fraction (of course, under global constraint of matter conservation) – absence of response to any change of phase fractions.** For correct account of compositional fluctuations in this case one should take into account the input of interfaces.

(2) Second reason of flux fluctuations (much less studied) is related to stochastic nature of structural defects which can be treated as the inevitable fluctuations of structure - dislocation density, grain sizes, interfaces curvatures. (2.1) First, such fluctuations lead to fluctuations of effective diffusivities (combinations of bulk diffusivity, grain-boundary and dislocation diffusivity). (2.2) Second, climbing of dislocations leads to complicated spatial and time-dependent distribution of drifts. (2.3) Third, gradients of curvatures between neighboring two-phase cells lead to additional local fluxes generated by capillary forces. All these fluctuations of the second type may lead to non-zero random fluxes with typical spatial scale up to microns

As a simple example of the second type flux fluctuations, one may consider coarsening: Indeed, imagine some very fine-dispersed two-phase alloy (for example, eutectic alloy with submicron lamellar structure). Let us choose, say, 5 micron as a size of two-phase cell. Initially, any such cell has a lot of particles of both phases. After long enough coarsening many such cells will contain only alpha- or only beta-phases. It means that coarsening leads to mutual transfer (actually, exchange) of phases between cells.

Detailed study of all possibilities leading to flux fluctuations, is a special interesting problem which will be discussed elsewhere. Here we will just postulate some level of noise – dispersion of random fluxes between neighboring two-phase cells. Most probably, at least the noise of second type has some "memory" – substantial time correlations, since it is related to the motion of mesoscopic objects (grain boundaries, interfaces, dislocations…). In this paper we limit ourselves to the noise without memory.

The main peculiarity of noise in the two-phase mixture is that spatial redistribution of phases, with preservation of local equilibrium between phases, does not cause any "back-force". Thus, random redistributions of phase fractions between neighboring two-phase cells create gradients of mean concentrations but not the gradients of chemical potentials. So, behavior of any two-phase cell in the composition space should be like random walk without any "wind". Hence, as a result of such random walk, system will have some, changing in time, distribution of volume fractions, $f(p_\beta)$, satisfying two constraints:

Normalization condition -
$$\int_0^1 f(p_\beta)\, dp_\beta = 1, \tag{6}$$
and matter conservation condition
$$\int_0^1 p_\beta f(p_\beta)\, dp_\beta = < p_\beta > = \frac{v^\beta}{v^\alpha + v^\beta}. \tag{7}$$

The width of such distribution surely depends on the chosen size of two-phase cells. The larger are the cells - the more narrow is the distribution.

Natural question is - will this distribution, under continued noise and fixed size of two-phase cells, tend to some steady-state function. If so, what will be this steady-state distribution in the phase fractions space.

To answer these questions, we start from a simplified model example (Section II), and then try to formulate the problem for the case of interdiffusion in the two-phase regions of the ternary system. (Section III).

II. Model of random walk of the binary two-phase system along the conode

Consider 3D system consisting of N*N*N cubic two-phase cells. Let *i* be an index of some fixed cell, and *in* is an index of one of its neighbors. Let fluctuations lead to random exchange between these cells:

$$p_\beta new(i) = p_\beta(i) - \Delta p_\beta(i \to in), p_\infty new(i) = p_\infty(i) + \Delta p_\infty(i \to in) \qquad (8)$$

$$p_\beta\, new(in) = p_\beta(in) - \Delta p_\beta(i \to in), \; p_\infty new(in) = p_\infty(in) - \Delta p_\beta(i \to in), \qquad (9)$$

$$\Delta p_\alpha(in \to i) = \Delta p_\beta(i \to in). \qquad (10)$$

Evidently, the volume fractions cannot be negative neither be larger than 1. So, the atomic fraction of some phase transferring from one cell to another, should be small if the existing atomic fraction is small. To provide this property, in our algorithm, after randomly choosing the cell and its neighbor, we first randomly determine in what direction the phase beta will be transferred. If, according to this random choice, beta phase should be transferred from *i* to *in,* that is, if $\Delta p_\beta(i \to in) > 0$, then we randomly find the magnitude of transfer as

$$\Delta p_\beta(i \to in) = p_\beta(i) \cdot p_\infty(in) \cdot dp0 \cdot random == p_\beta(i) \cdot \left(1 - p_\beta(in)\right) \cdot dp0 \cdot random. \,(11)$$

In our model example, so far, we treated the factor dp0 as constant.

At Figure 1 a,b,c we present the steady-state distributions which correspond to three different values of dp0 (0.1, 0.2 and 0.3)
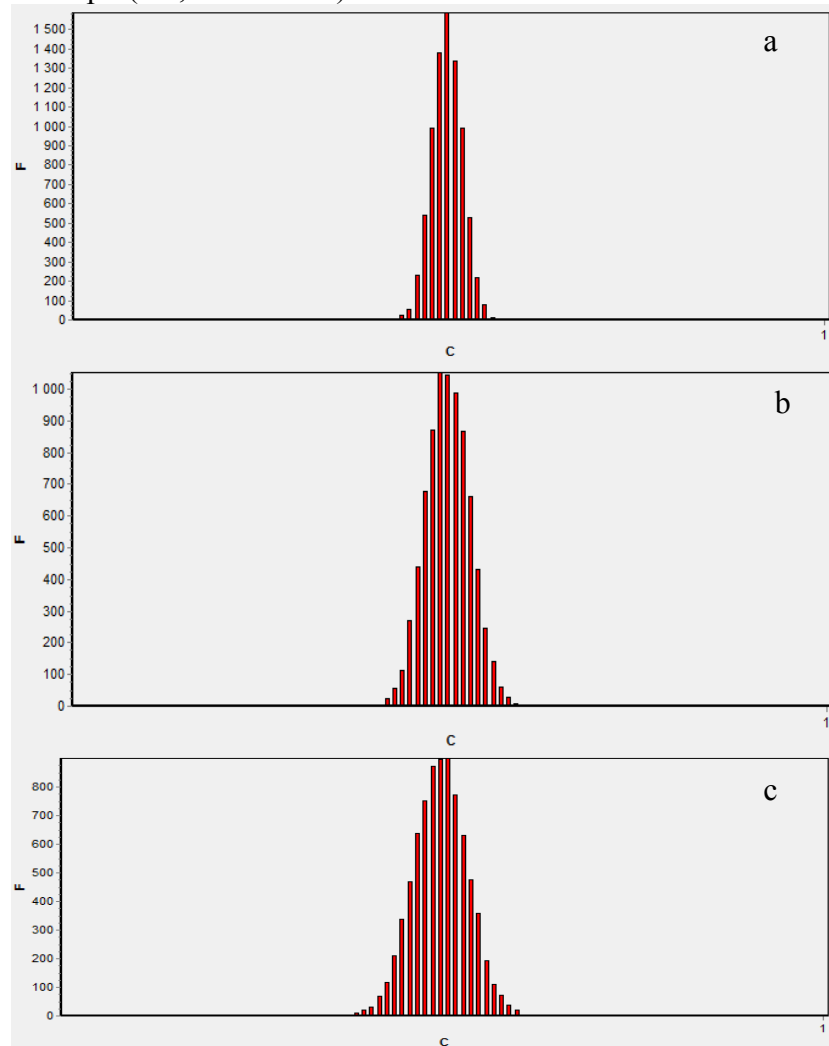

Fig.1. Steady-state distributions of compositions under various amplitude of random walk step a – dp0=0.01, b – dp0=0.02, c – dp0=0.03.

As one may see at Fig.1a,b,c, the distribution tends to some steady-state shape, depending on the magnitude of dp0.

III. Stochastization of the diffusion path in the two-phase region of the ternary systems

Consider the initial single-phase non-equilibrium ternary alloy (diffusion couple) consisting of two regions of volumes V_L, V_R with concentrations $(C_1^L, C_2^L), (C_1^R, C_2^R)$.

After long annealing, "at the end of the day", the full homogenization will be reached. In the final state the homogeneous alloy is formed with uniform composition:

$$C_i^{(F)} = (V_L C_i^L + V_R C_i^R)/(V_L + V_R), \; i = 1,2 \qquad (12)$$

The situation becomes more complicated with two-phase alloys (Fig. 2).

Consider, the points C^L, C^L are in the two-phase region of concentrations' triangle. In the final state the average concentration $\overline{C_{(F)}} \equiv (\overline{C_1}, \overline{C_2})$ is determined by the equalities (12), but, in a general case, alloy in its final state must not be a homogeneous one. For example, it may consist of of two regions 1 and 2, which are in equilibrium, the average concentrations of which being on one and the same conode with the point of average state and the volume fractions are bound with correlations:

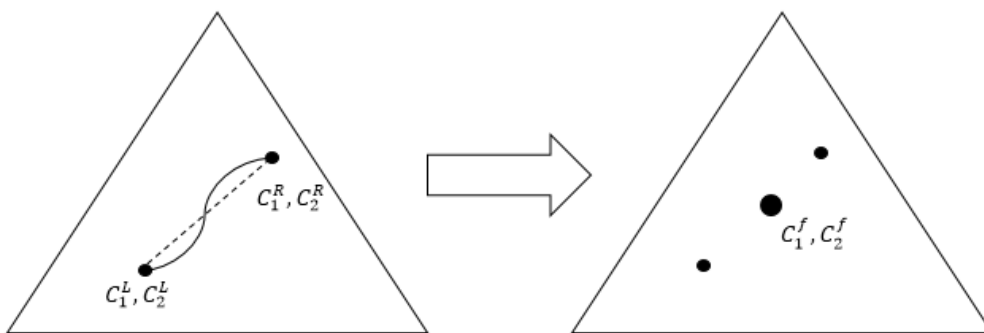$$p(\vec{F}) = (V_L p(1) + V_R p(2))/(V_L + V_R) \qquad (13)$$

Fig.2. Scheme of diffusion path evolution in concentration triangle for the single-phase diffusion couple.
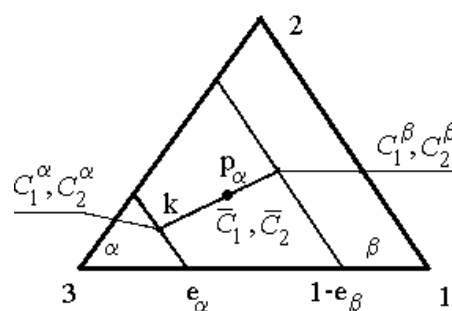

Fig. 3. Schematic isothermal section of ternary phase diagram with two-phase region.

Apparently, in the final state the stratification is possible into arbitrary quantity of regions on one and the same conode, with the normalizing condition maintained (12).

All terminal states are thermodynamically equivalent, they correspond to the identical average all volume concentrations and in this sense they are equal. The main difference from the one-phase region is laid in this indefiniteness. Naturally we should expect that the indefiniteness of the final balanced state would influence the specific solutions of diffusion

equations in the two-phase region, describing the system relaxation to the equilibrium. As demonstrated in [1, 3], if we use the effective interdiffusion matrix for the description of interdiffusion in two- phase regions, then we can use well-known equations but with an important constraint – zero determinant of interdiffusivity matrix:

$$\frac{\partial c_i}{\partial t} = \frac{\partial}{\partial x}\left(\sum_{k=1}^{2} D_{ik}\frac{\partial c_k}{\partial x}\right) \tag{14}$$

$$D_{12}D_{21} = D_{11}D_{22}$$

Degeneracy of effective diffusivity matrix leads to non-trivial behavior of diffusion path [4-11]. We suggest to add the noise to these equations:

$$\frac{\partial c_i}{\partial t} = -\frac{\partial}{\partial x}\left(-\sum_{k=1}^{2} D_{ik}\frac{\partial c_k}{\partial x} + White\ Noise\ of\ i - Flux\right) \tag{15}$$

$$D_{12}D_{21} = D_{11}D_{22}$$

It is convenient to make experiments for a different stochastic model with white noise replaced by noise with step-wise probability distribution $\frac{A_i}{\sqrt{dt}}\sqrt{3}\cdot(2\cdot random - 1)$.

$$\frac{\partial c_i}{\partial t} = \frac{\partial}{\partial x}\left(\sum_{k=1}^{2} D_{ik}\frac{\partial c_k}{\partial x} - \frac{A_i}{\sqrt{dt}}\sqrt{3}\cdot(2\cdot random - 1)\right) \tag{16}$$

$$D_{12}D_{21} = D_{11}D_{22}$$

Here the factor $\sqrt{3}$ provides the unit dispersion of the random function $\sqrt{3}\cdot(2\cdot random - 1)$ ($<(2\cdot random - 1)^2> = \int_{-1}^{1} x^2 f(x)dx = \int_{-1}^{1} x^2 \frac{1}{2} dx = \frac{1}{3}$). The random variable *random* clearly depends on time *t*, and has a uniform distribution on [0,1]. Zero stability along each conode should influence the solutions of equations (16). An analysis of such solutions will be made elsewhere. In our future research we intend to enhance our stochastic model, taking into account conodes and concentrations' triangle.
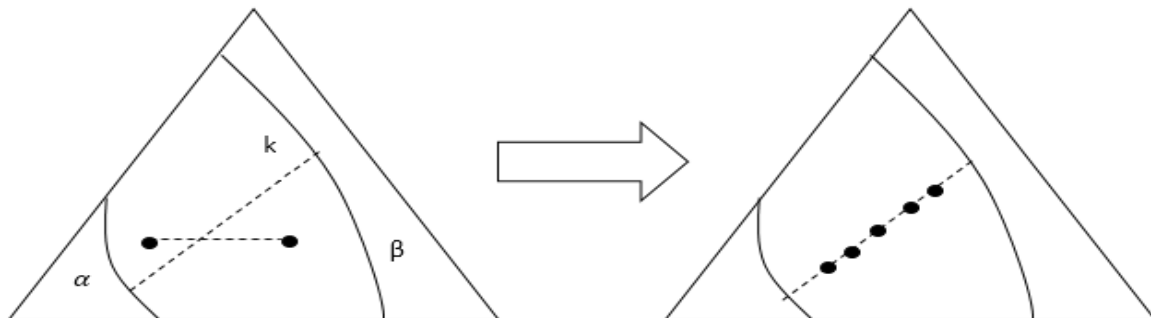

Fig.4. Possibility of stratification. In the two-phase region.

Conclusion

Equalizing of chemical potentials for each component in the two-phase system is not a last step of evolution. In general case, it should be followed by the random walk of "physically small" two-phase cells along conode within the composition space. This random effect may be not only the last stage of interdiffusion but, as well, may influence the diffusion path evolution during interdiffusion in the ternary or multicomponent system.

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Анотація. А. Гусак, Г. Лещинський, М. Данілевський, В. Клочай. Нульова стійкість двофазних систем і випадкові блукання у просторі концентрацій. Розглянуті можливості нестабільності та випадкових блукань вздовж коноди всередині двофазних областей простору концентрацій для бінарних і потрійних систем. Запропоновані деякі прості моделі вказаного випадкового блукання.
Ключові слова: дифузія, флуктуації, двофазний сплав, конода, випадкові блукання

УДК 53.09   PACS 34, 61, 77, 81, 88

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АВТОМАТИЗАЦІЯ МЕТОДУ КОРЕЛЯЦІЙНОЇ СЕЛЕКЦІЇ ПЕРОВСКІТІВ

Запропоновано підхід, який дозволяє автоматизувати відбір перовскітних сполук ABO_3, які не мають необхідних властивостей. Спочатку здійснюється процедура визначення кореляційних залежностей «властивість – склад сполуки». У цій роботі досліджувались сполуки з високим рівнем іонної провідності (σ). Обговорюються особливості відомих дескрипторів в оптимізації параметрів перовскітів ABO_3. В розрахунках кореляційних залежностей ми використали дескриптор, який містить в собі співвідношення іонних радіусів R_A/R_B та потенціалів іонізації V_A/V_B для катіонів A і B. Кореляційні залежності між дескриптором і величиною σ аналізували за допомогою спеціальної комп'ютерної програми, яка була розроблена для селекції перовскітів, що забезпечують відповідні коефіцієнти кореляції, тобто достатньо високі значення іонної провідності.
Ключові слова: перовскіти, іонна провідність, дескриптор, кореляційна залежність, регресійний аналіз, комп'ютерне моделювання.

1. Вступ

Фізичні та хімічні властивості, а також функціональні характеристики перовскітних матеріалів дуже чутливі до їх елементного складу. Тому для вдосконалення і модифікації перовскітних матеріалів потрібні тривалі експериментальні та теоретичні дослідження. В останній час при дослідженні