

CRYSTAL-LATTICE DEFECTS

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Two Remarks on Wagner Integrated Diffusion Coefficient

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Integrated interdiffusion coefficient, introduced by Carl Wagner in 1969, is revisited. First, it is applied for the whole diffusion zone, consisting of solid solutions and/or layers of intermediate compounds. We demonstrate, for the first time, that the Wagner coefficient satisfies the simple additive rule: the total squared inter-penetration width is proportional just to the sum of all Wagner coefficients of all intermediate phases of the system. Second, we check the applicability of Wagner coefficients in the atomistic-scale modeling of reactive diffusion. Checking is done for the growth of intermediate compound AB with BCC lattice.

Key words: diffusion, reaction, Wagner diffusion coefficient, parabolic Boltzmann–Matano substitution, stochastic kinetic mean field method.

В даній статті заново аналізується інтегральний коефіцієнт взаємної дифузії, введений Карлом Вагнером ще у 1969 році. По-перше, він застосовується для всієї дифузійної зони, яка складається з твердих розчинів та/або шарів проміжних сполук. Ми вперше показуємо, що коефіцієнт Вагнера задовольняє простому адитивному правилу: квадрат ширини взаємопроникнення пропорційний просто сумі всіх коефіцієнтів Вагнера всіх проміжних фаз системи. По-друге, ми перевіряємо застосовність коефіцієнтів Вагнера при моделюванні реакційної дифузії на атомному масштабі. Перевірка проводиться для росту проміжної фази АВ з ОЦК решіткою.

Ключові слова: дифузія, реакція, коефіцієнт дифузії Вагнера, параболіч-

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на підстановка Больцмана–Матано, стохастичний метод кінетичного середнього поля.

В данной статье анализируется интегральный коэффициент взаимной диффузии, который был введен Карлом Вагнером ещё в 1969 году. Во-первых, он применяется ко всей диффузионной зоне, которая состоит из твёрдых растворов и/или слоёв промежуточных соединений. Мы впервые показываем, что коэффициент Вагнера удовлетворяет простому аддитивному правилу: квадрат ширины взаимопроникновения пропорционален просто сумме всех коэффициентов Вагнера всех промежуточных фаз системы. Во-вторых, мы проверяем применимость коэффициентов Вагнера при моделировании реакционной диффузии в атомном масштабе. Проверка производится для роста промежуточной фазы АВ с ОЦК решёткой.

Ключевые слова: диффузия, реакция, коэффициент диффузии Вагнера, параболическая подстановка Больцмана–Матано, стохастический метод кинетического среднего поля.

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1. INTRODUCTION

Joining of two materials by interdiffusion or by reactive diffusion is a complicated process involving diffusion, lattice flow, stress generation, and relaxation, chemical reactions *etc.* The main, integrated characteristic of joining is a mean depth of mutual penetration. Below we suggest the very simple measure of the joining magnitude and its interrelation with Wagner integrated diffusion coefficients. Integrated diffusion coefficient was introduced by Carl Wagner, and is commonly used to simplify the kinetic description of the intermediate phases with a narrow concentration range (compounds) growing in the diffusion zone [1–6]. Very often, the concentration range of growing compounds is so narrow that it is difficult to measure it, and even more difficult to measure the concentration gradient inside the compound layer. Formally speaking, one may encounter the mathematical uncertainty of the type ‘infinity multiplied by zero’ in the formulation of the first Fick’s law for the interdiffusion flux density across the growing compound layer [7]:

$$\Omega J_B = -\tilde{D} \frac{\partial N_B}{\partial X} \approx -\frac{\bar{D} \Delta N_B}{\Delta X}, \quad (1)$$

where Ω —atomic volume, N_B —an atomic fraction of component B in the binary alloy, \tilde{D} —average interdiffusion coefficient.

In the product $\bar{D} \Delta N$ for the ‘line’ (or ‘point’) compound, the homogeneity range tends to zero, $\Delta N \rightarrow 0$ and average interdiffusivity

tends to infinity,

$$\bar{D} = \langle (N_A D_B^* + N_B D_A^*) \frac{N_A N_B}{kT} \frac{\partial^2 g}{\partial N_B^2} \rangle \rightarrow \infty, \quad (2)$$

due to thermodynamic factor $\varphi \equiv \frac{N_A N_B}{kT} \frac{\partial^2 g}{\partial N_B^2}$ (g —Gibbs free energy per atom) tending to infinity at $\Delta N \rightarrow 0$ inversely proportionally to ΔN . Luckily, in most cases, we are not interested in the details of concentration dependence inside the intermediate phases, but instead, need just prediction of the growth kinetics. And this kinetics is determined by the Wagner integrated diffusion coefficient

$$D_w(\text{phase } k) = \int_{\Delta N(k)} \bar{D}(N) dN. \quad (3)$$

Substituting Eq. (2) into integral (3) one easily gets [5]:

$$\begin{aligned} D_w(\text{phase } k) &\approx \\ &\approx \frac{N(k)(1-N(k))(N(k+1)-N(k-1))}{(N(k+1))(-N(k))(N(k)-N(k-1))} \frac{(D_A^* N_B + D_B^* N_A)_k}{k_B T} \times \\ &\times \Delta g(k-1, k+1 \rightarrow k). \end{aligned} \quad (4)$$

Here $\Delta g(k-1, k+1 \rightarrow k)$ is a thermodynamic driving force of reaction ($k-1, k+1 \rightarrow k$), $N(k)$ is an average molar fraction of B in the k -th intermediate compound. Equation (4) has the traditional structure of the product ‘mobility times driving force’.

In the following Section 2 the Wagner coefficient is generalized over the total diffusion zone and related (by Matano–Boltzmann substitution) to the mean squared interpenetration depth. In Section 3 we modify the standard Matano analysis to get explicit expression for measuring the Wagner diffusivity within single phase. In Section 4 we check the applicability of Wagner coefficient to the mean-field atomistic-scale model of phase growth (SKMF–Stochastic Kinetic Mean Field). Namely, we model the reactive growth of B2 phase in the diffusion couple A–B with b.c.c. lattice and account of two coordination shells.

2. INTEGRATED DIFFUSION COEFFICIENT OVER THE WHOLE DIFFUSION ZONE

Let us consider the general case of the binary diffusion couple with the step-wise initial profile based on the Heaviside step function:

$$N(t=0, X) = N_L + (N_R - N_L)\theta(X - X_M), \quad (5)$$

$$\theta(X - X_M) \equiv \begin{cases} 0, & X < X_M, \\ 1, & X > X_M. \end{cases}$$

Here X_M is a coordinate of Matano plane (initial contact plane in the laboratory reference frame). Interdiffusion coefficient can be one continuous function of composition (full solubility) or several step functions with zero gaps between them (limited solubility and possibly the intermediate phases). It is a well-known trick to prescribe zero interdiffusivity to the two-phase regions. Indeed, any two mixtures of two neighbouring phases in mutual equilibrium with different average compositions have the same chemical potential of any species in both phases and therefore, zero flux. Under such conditions one expect the concentration profile to be monotonic, and satisfy the parabolic Boltzmann–Matano substitution:

$$\begin{aligned} \frac{\partial N}{\partial t} &= \frac{\partial}{\partial X} \left(\tilde{D}(N) \frac{\partial N}{\partial X} \right), \\ N(t, X) &= N \left(\xi = \frac{X - X_M}{\sqrt{t}} \right) \Rightarrow -\frac{1}{2} \xi \frac{dN}{d\xi} = \frac{d}{d\xi} \left(\tilde{D}(N) \frac{dN}{d\xi} \right). \end{aligned} \quad (6)$$

Now let us multiply both sides of Eq. (6) by ξ and integrate over whole couple length (formally infinite) corresponding to initial concentration range (N_L, N_R):

$$-\frac{1}{2} \int_{-\infty}^{\infty} \xi^2 \frac{dN}{d\xi} d\xi = \int_{-\infty}^{\infty} \xi \frac{d}{d\xi} \left(\tilde{D}(N) \frac{dN}{d\xi} \right) d\xi. \quad (7)$$

Elementary transformation of both sides gives:

$$\begin{aligned} -\frac{1}{2} \int_{N_L}^{N_R} \xi^2 dN &= \xi \tilde{D}(N) \frac{dN}{d\xi} \Big|_{-\infty}^{\infty} - \int_{-\infty}^{\infty} \left(\tilde{D}(N) \frac{dN}{d\xi} \right) d\xi = \\ &= 0 - \int_{N_L}^{N_R} \tilde{D}(N) dN = -D_w(N_L, N_R). \end{aligned} \quad (8)$$

Coming back to time and space parameters t, X , one gets the following parabolic law for the squared width of whole diffusion zone:

$$\langle (X - X_M)^2 \rangle \equiv \frac{1}{N_R - N_L} \int_{N_L}^{N_R} (X - X_M)^2 dN = \frac{2D_w(N_L, N_R)}{N_R - N_L} t, \quad (9)$$

where $D_w(N_L, N_R) \equiv \int_{N_L}^{N_R} \tilde{D}(N) dN$ —generalized Wagner diffusion coef-

ficient over the total couple. In particular case of the couple A–B with n intermediate compounds and limited solutions of B in A (α) and A in B (β) one gets:

$$\langle (\Delta X)^2 \rangle = 2 \left(\int_0^{N_\alpha} \tilde{D}(N) dN + \sum_{k=1}^n \int_{(\Delta N(k))} \tilde{D}_k(N) dN + \int_{N_\beta}^1 \tilde{D}(N) dN \right) t. \quad (10)$$

The just obtained new equations (9), (10) seem to be physically clear, but, to the best of our knowledge, they had not been published. These equations can be interpreted as a kind of ‘addition rule’ or ‘superposition rule’ for mean squared interdiffusion depth: the inputs of all intermediate phases into the mean squared interdiffusion depth are just added. In its turn, the mean squared interdiffusion depth seems to be the natural measure of joining between two materials. Of course, these conclusions are valid only for the diffusion-controlled, parabolic stage of inter- and reactive diffusion.

3. MODIFICATION OF MATANO SCHEME FOR DIRECT CALCULATION OF THE WAGNER DIFFUSIVITY OVER SINGLE PHASE

Let us consider the diffusion couple composed of two samples of the same intermediate phase but with compositions N_L , N_R corresponding to the left and right margins of the homogeneity concentration range of this very phase. Interdiffusion in such couple leads to some concentration profile and to well-known Matano expression for the local diffusivity:

$$\tilde{D}(N) = - \frac{1}{2t (dN/dx)|_C} \int_{N_L}^N (x - x_M) dN, \quad x_M = \frac{1}{N_R - N_L} \int_{N_L}^{N_R} x dN. \quad (11)$$

Now we integrate (11) over the concentration range and get the direct Matano expression for Wagner diffusivity:

$$D_W \equiv \int_{N_L}^{N_R} \tilde{D}(N) dN = \frac{1}{2t} \int_{x_L}^{x_R} dx \int_{N_L}^{N(x)} (x_M - x(N')) dN'. \quad (12)$$

For the array of atomic planes with mean-field concentrations $C[i]$ it translates into following algorithm:

$$\begin{aligned} x[i+1] - x[i] &= dx, \\ iM &\equiv \sum_{i=iL}^{iR-1} i(N[i+1] - N[i]) / (N_R - N_L), \end{aligned} \quad (13)$$

$$D_w = \frac{(dx)^2}{2t} \sum_{i=iL}^{iR-1} \sum_{j=iL}^{i+1} (iM - j)(N[j+1] - N[j]).$$

4. CHECK BY COMPUTER EXPERIMENT: COMPARISON OF TWO WAYS OF EVALUATION OF THE WAGNER COEFFICIENT FOR THE GROWTH OF B2-PHASE LAYER IN THE DIFFUSION COUPLE

To illustrate and check the above-mentioned results, we will use atomistic Kinetic Mean Field (KMF) method for the modelling of atomic migration and diffusion-controlled phase transformations on the rigid lattice, suggested by George Martin [8], applied to strongly asymmetric thin-film couples in [9–11] and generalized to 3D in [12]. It was developed to include noise, for modelling nucleation and other processes related to overcoming the nucleation barriers [12–15]. The generalized version of KMF was called SKMF (Stochastic Kinetic Mean Field). This method seems to be most effective for the coarsened space and time scales, intermediate between phenomenological method (microns and larger scale) and Kinetic Monte Carlo (first of all, nanoscale). Contrary to Monte Carlo, SKMF cannot predict, say, the correlation factors for vacancy diffusion, but, on the other hand, it enables the atomistic description of reactive phase layer growth for tens of nanometres much easier and faster than by MC. We will see it just now. Let us consider the ordered B2 phase layer formation in the b.c.c. diffusion couple A–B. In the mean-field approximation with rigid lattice, the ordering of B2 structure is a second-order phase transition. In such case, the interdiffusion cannot provide the formation and growth of the ordered layer with almost constant composition (concentration plateau). On the other hand, typical technologically important examples of B2 phases, like NiAl, CoAl, FeAl, AuZn, CuZn *etc.* are the very distinct intermediate phases (compounds), separated from neighbouring phases by quite measurable concentration gaps. To make the phase diagram of our model b.c.c.-system more realistic, we use (everywhere below) the approximation of interactions in two coordination spheres ($Z1=8$, $Z2=6$).

For simulation we chose the following parameters. Temperature: 750 K. Interaction energies: $V_{AA}^I = V_{BB}^I = -10^{-21} J$, $V_{AB}^I = -3,9 \cdot 10^{-21} J$, $V_{AA}^{II} = V_{BB}^{II} = -8,76 \cdot 10^{-21} J$, $V_{AB}^{II} = -2 \cdot 10^{-21} J$.

4.1. Phase Diagram (Equilibrium Concentrations) Construction by the Diffusion Couple Method

First of all, we use KMF-equations without noise [8, 12] for determining the equilibrium concentrations

$$\frac{dN_i}{dt} = -\sum_{j=1}^Z \left[N_i(1 - N_j)\Gamma_{i,j}^{\text{mean-field}} - N_j(1 - N_i)\Gamma_{j,i}^{\text{mean-field}} \right], \tag{14}$$

where

$$\Gamma_{i,j}^{\text{mean-field}} = \Gamma_0 e^{-\overline{E_{i,j}}/(k_B T)}. \tag{15}$$

Energies are calculated in the middle field approximation for the two coordination spheres:

$$\begin{aligned} \overline{E_{i,j}} = & (M^I - V^I) \sum_{l=1}^{Z^I=12} C_l + (M^I + V^I) \sum_{n=1}^{Z^I=12} C_n + (M^{II} - V^{II}) \sum_{l=1}^{Z^{II}=6} C_l + \\ & + (M^{II} + V^{II}) \sum_{n=1}^{Z^{II}=6} C_n, \end{aligned} \tag{16}$$

$$M^{I(II)} = \frac{V_{AA}^{I(II)} - V_{BB}^{I(II)}}{2} \text{---asymmetry parameters for two shells,}$$

$$V_{AB}^{I(II)} = V_{AB}^{I(II)} - \frac{V_{AA}^{I(II)} + V_{BB}^{I(II)}}{2} \text{---mixing energies, } \Gamma_0 = 9e^{\frac{-E_0 + Z^I(V_{AB}^I + V_{BB}^I) + Z^{II}(V_{AB}^{II} + V_{BB}^{II})}{k_B T}}$$

(9 — attempts frequency, E_0 —saddle-point energy, taken in KMF the same for all jumps).

We construct diffusion couples A–AB and AB–B and simulate diffusion until full equilibrium meaning stationary concentration steps (Fig. 1).

Boundary concentrations (mole fraction of species A) obtained by diffusion couples (A–AB, AB–B) at the temperature 750 K, after averaging over each pair of atomic planes (100) are: 0.943, 0.585, 0.415, 0.057.

4.2. Phase Growth in A–B-Couple

Introduction of interactions within the second coordination shell makes the ordering in stoichiometric AB alloy the first order transformation needing the overcoming of the nucleation barrier. In principle, one can provide the nucleation by choosing initial condition with sufficient extra free energy. Yet, more natural is to provide the possibility of fluctuations. Therefore, everywhere below we introduce the noise of local fluxes between neighbouring sites in the form of the noise of jump frequencies and use SKMF instead of KMF method, with the following main kinetic equations [13–15]:

$$\frac{dN_i}{dt} = -\sum_{j=1}^Z [N_i(1 - N_j)(\Gamma_{i,j}^{\text{mean-field}} + \delta\Gamma_{i,j}^{\text{Lang}}) - \tag{17}$$

$$\begin{aligned}
 & -N_j(1 - N_i)(\Gamma_{j,i}^{\text{mean-field}} + \delta\Gamma_{j,i}^{\text{Lang}})], \\
 & \delta\Gamma_{i,j}^{\text{Lang}} = \frac{A_n}{\sqrt{dt}} \sqrt{3}(2\text{random} - 1), \tag{18}
 \end{aligned}$$

Dt —non-dimensional time-step, $A_n = 0.01$ (see Figs. 2 and 3).

The squared thickness of the intermediate phase versus time, after some time averaging, corresponds to the parabolic law (Fig. 4).

As known from the diffusion textbooks [2, 5, 7], the kinetics of single IMC parabolic growth is described by the equation

$$(\Delta X)^2 = \frac{2D_w}{N_{IMC}(1 - N_{IMC})} t \approx 8D_w t (N_{IMC} = 1/2). \tag{19}$$

Comparison of Eq. (19) with Fig. 4 ($\Delta x^2(m^2) = 6.23 \cdot 10^{-12}(m^2/s)t(s)$) gives:

$$D_w = \frac{6.23 \cdot 10^{-12}}{8} \approx 7.8 \cdot 10^{-13} \frac{m^2}{s}. \tag{20}$$

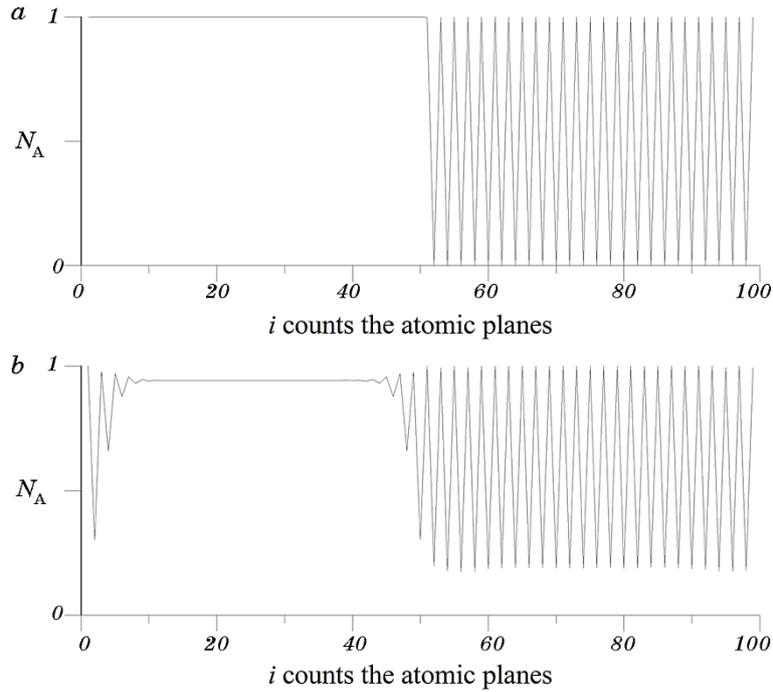


Fig. 1. Typical initial (a) and final (b) concentration profiles in the couple A-AB, without noise.

4.3 Finding of Wagner Diffusivity from the Computer Experiment with Diffusion Couple within the Homogeneity Range of AB-Phase

Now we construct the diffusion couple 0.415–0.585 within the homogeneity range of AB-phase at 750 K. The typical profile after some time of annealing and averaging over each two atomic planes (100) is shown at Fig. 5.

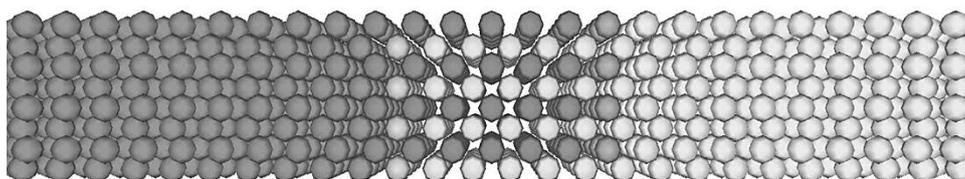


Fig. 2. General picture of the AB phase formation in the couple A–B. Colour of each site corresponds to local probability (atomic fraction) of sort A at this site.

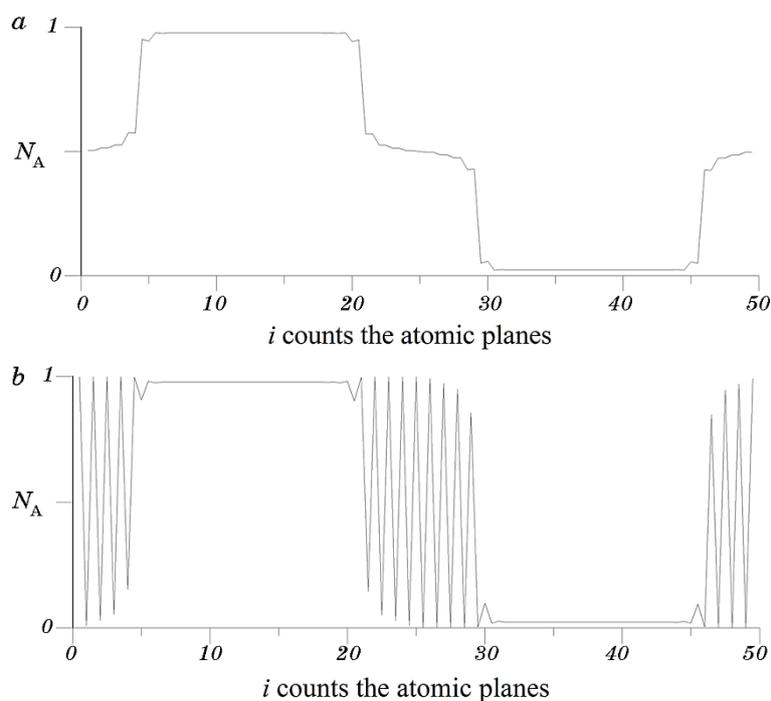


Fig. 3. Concentration profile along X -axis, obtained by averaging over Y and Z . With additional averaging over each two planes (a), without averaging over each two planes (oscillations mean sublattices) (b). We observe two layers of the ordered phase due to the periodic boundary condition for the thin-film system.

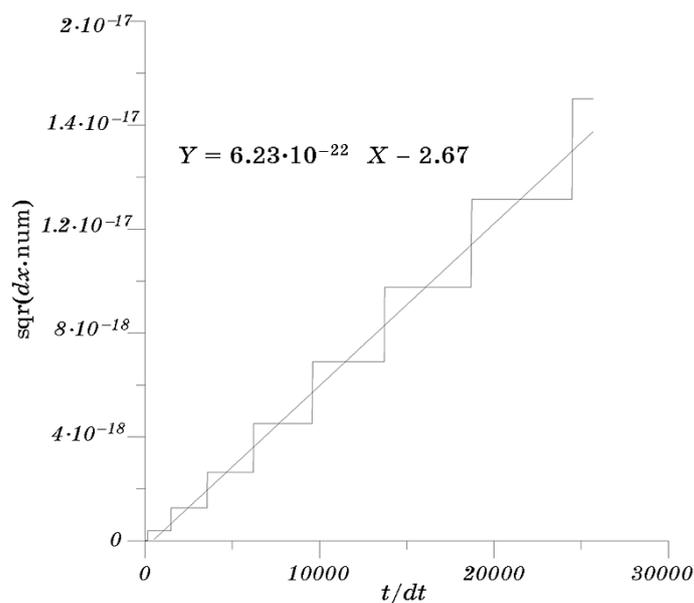


Fig. 4. Growth of the AB phase over time.

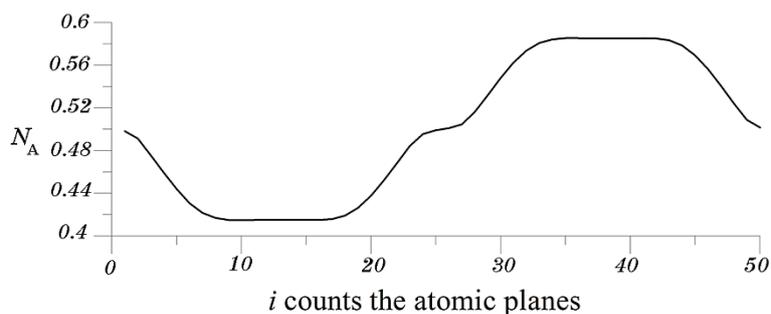


Fig. 5. Profile of the couple $N_L - N_R$ within the homogeneity range.

We calculate the Wagner interdiffusivity now from the interdiffusion in this limited diffusion couple, according to Eq. (13). It gives $D_w = 8.8 \cdot 10^{-13} \text{ m}^2/\text{s}$, which is rather close to Eq. (20) obtained by alternative method (kinetics of reactive growth).

5. SUMMARY

Thus, the concept of Wagner integrated diffusion coefficient is generalized from the individual compounds to the whole diffusion zone of the arbitrary diffusion couple. This generalized concept is applied to

broad solid solutions (Eq. (9)) as well as to the sequence of compounds with a narrow homogeneity range (Eq. (10)). Independently it can be calculated for each intermediate phase by the modified Matano equation (13). Results are checked within atomistic SKMF model.

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