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MACIEJ ORGANIŚCIAK, MAREK IZDEBSKI, RAFAŁ LEDZION

Institute of Physics, Lodz University of Technology, ul. Wólczańska 219,
90-924 Łódź, Poland, e-mail: izdebski@p.lodz.pl

ANALYTICAL KINETIC BLOCK MODEL OF CRYSTAL-MOTHER-PHASE MULTILAYER INTERFACE

Simple kinetic block model of multilayer crystal-mother-phase interface is proposed. The model leads to a system of differential equations which can be solved without the need to run Monte Carlo simulations. The proposed model is based on Bragg-Williams approximation (called also zeroth-order approximation), "solid-on-solid" assumption, and other assumptions common with thermodynamic Temkin model. Thus, it is possible to test the compliance of kinetic and thermodynamic approaches in a situation where all other significant differences between models are eliminated. Moreover, a comparison with the results of kinetic Monte Carlo simulations allows for better understanding of the impact of Bragg-Williams approximation.

Keywords: crystal-mother-phase interface, Temkin’s model, kinetic block model, Bragg-Williams approximation.

1. INTRODUCTION

The block models of crystal-mother-phase interface, which are known from the literature, can be divided into two groups: thermodynamic models in which the minimum of free energy of the system is studied and kinetic models where time evolution of the interface is considered as a sequence of creations and annihilations of solid blocks on the crystal surface. Among the best known thermodynamic models are the single-layer Jackson model [1-3], two-layer Mutaftschiev model [4], and Temkin model which does not limit the number of layers in the interface [5, 6]. Today, there exist many variants of kinetic models which are used mainly as a basis for performing kinetic Monte Carlo (MC) simulations (see, e.g., Refs. [7-10]). Both groups of models lead to distinction between continuous growth and layer growth mechanism. However, the conditions for specific growth mechanism predicted by thermodynamic models are not consistent with those obtained from MC simulations [2, 11, 12]. Unfortunately, it is difficult to draw clear conclusions about this inconsistency when the effects of at least two fundamental differences may be important: 1) thermodynamic versus kinetic approach, 2) the zeroth-order mean field or Bragg-Williams approximation used in the thermodynamic models versus long-range ordering of solid blocks included in the kinetic MC simulations. Here, the zeroth-order approximation means that a solid cell in the solid-fluid mixture is surrounded on average by the same number of solid and fluid cells as the average composition of the whole layer.

Recently, a simple kinetic single-layer model was proposed in Ref. [11], which is based on the fundamental assumptions proposed yet in the Jackson model, including also the zeroth-order approximation. The model leads to a single equation, which could be solved without the need for performing MC simulations. It was shown that the kinetic and thermodynamic approaches lead to very similar predictions about the growth mechanism when all other fundamental differences between models are removed.

The aim of this study is to generalize the kinetic single-layer model from Ref. [11]. In our improved model, the number of layers in the solid-fluid interface is no longer limited, while the zeroth-order approximation is still used. The generalization proposed in this work is inspired by the generalization made earlier in the thermodynamic models, where more general Temkin's expressions lead to Mutaftschiev's or Jackson's expressions when the number of layer in the interface is limited [6]. Comparison of the results obtained using our multilayer kinetic model and the Temkin model allows one to test the compatibility of fundamentally different kinetic and thermodynamic approaches when all other assumptions are as close as possible. Moreover, confrontation of our generalized kinetic zeroth-order model and kinetic MC simulations allows a better understanding of the impact of zeroth-order approximation. This work is based on a study carried out in the framework of engineering thesis [13].

2. THERMODYNAMIC TEMKIN MODEL

In this work we follow the Temkin model in the formulation presented by Gilmer and Bennema in Ref. [6]. Because we will often refer to this model, we briefly describe it below.

In the Temkin model, a completely flat interface placed between the $n = 0$ and $n = 1$ layers is considered as a reference state. The change in the Gibbs free energy due to roughening of this surface is given by

$$\Delta G = \Delta G_{\mathrm{f-s}} + \Delta U_{\mathrm{mix}} - T\Delta S_{\mathrm{mix}} , \tag{1}$$

where $\Delta G_{\mathrm{f-s}}$ is the change in Gibbs free energy due to the replacement of solid blocks with chemical potential μ_{s} by fluid blocks with chemical potential μ_{f} in the layers $n \le 0$ and vice versa in the layers $n \ge 1$. Hence, the change for the whole interface, where the number of layers is not limited, is given by [6]

$$\Delta G_{\mathrm{f-s}} = \Delta\mu N\left[\sum_{n=-\infty}^{0}(1-C_n) + \sum_{n=1}^{\infty} C_n\right], \tag{2}$$

where $\Delta\mu = \mu_{\mathrm{f}} - \mu_{\mathrm{s}}$, N is the total number of cells in one layer, and $C_n = N_{ns}/N$ is the fraction of solid blocks in the n-th layer.

The symbols ΔU_{mix} and ΔS_{mix} in Eq. (1) are the energy and the entropy resulting from mixing of the two phases which were separated in the reference state. From the energetic point of view, this means replacing solid-solid bonds (with an energy ϕ_{ss}) and fluid-fluid bonds (ϕ_{ff}) by solid-fluid bonds (ϕ_{sf}). Since the creation of one solid-fluid bond requires breaking on average ½ solid-solid and ½ fluid-fluid bonds, the energy gain

$$\phi = \tfrac{1}{2}(\phi_{\mathrm{ss}} + \phi_{\mathrm{ff}}) - \phi_{\mathrm{sf}} . \tag{3}$$

The probability of finding a solid block at any given location in the n-th layer is C_n. As the Temkin model utilizes the zeroth-order (or Bragg-Williams) approximation, the probability of finding a fluid block at given position adjacent to this solid block is the same as the average probability of finding a fluid block in the n-th layer $(1 - C_n)$. Thus, the average number of solid-fluid bonds per one cell within the n-th layer is given by $4C_n(1 - C_n)$, where 4 is the coordination number for square lattice. Hence, the energy of mixing for the whole interface is [6]

$$\Delta U_{\mathrm{mix}} = 4\phi N \sum_{n=-\infty}^{\infty} C_n(1-C_n) . \tag{4}$$

According to Boltzmann's formula, the entropy of the interface $S = k \ln g$, where k is the Boltzmann constant and g is the number of configurations corresponding to a given macrostate. In the case of a perfectly flat interface $g = 1$, which implies that $S = 0$ for the reference state. After roughening of the interface, the configurations of the blocks in the $(n + 1)$-th layer allowed by the solid-on-solid assumption may differ only in the sites located above the solid blocks in the n-th layer. Among these NC_n locations there are NC_{n+1} indistinguishable solid blocks and $N(C_n - C_{n+1})$ fluid blocks so that the number of possible configurations in the $(n+1)$-th layer is

$$g_{n+1} = \frac{(NC_n)!}{(NC_{n+1})!\,[N(C_n - C_{n+1})]} \,. \tag{5}$$

Hence, the change in the entropy of the whole multilayer interface is given by [6]

$$\Delta S_{\mathrm{mix}} = k \ln(g) = k \ln \prod_{n=-\infty}^{\infty} \frac{(NC_n)!}{(NC_{n+1})!\,[N(C_n - C_{n+1})]} \,. \tag{6}$$

The use of Stirling's formula $\ln N! \approx N \ln N - N$ and the boundary conditions $C_{-\infty} = 1$ and $C_{+\infty} = 0$ allows the transformation of Eq. (6) into the form

$$T\,\Delta S_{\mathrm{mix}} = -kTN \sum_{n=-\infty}^{\infty} (C_n - C_{n+1}) \ln(C_n - C_{n+1}) \,. \tag{7}$$

Substitution of Eqs. (2), (4) and (7) into (1) gives the total change in the Gibbs free energy in the form

$$\begin{aligned} \frac{\Delta G}{NkT} &= \beta\left[\sum_{n=-\infty}^{0}(1 - C_n) + \sum_{n=1}^{\infty} C_n\right] + \alpha \sum_{n=-\infty}^{\infty} C_n (1 - C_n) + \\ &+ \sum_{n=-\infty}^{\infty} (C_n - C_{n+1}) \ln(C_n - C_{n+1}) \,, \end{aligned} \tag{8}$$

where the basic parameters α and β related to the conditions of crystal growth are given by

$$\alpha = 4\phi/kT, \tag{9}$$

$$\beta = (\mu_{\mathrm{f}} - \mu_{\mathrm{s}})/kT. \tag{10}$$

The interface is stable when the energy change ΔG has a minimum with respect to each C_n. The necessary condition for the existence of this minimum is

$$\frac{\partial(\Delta G / NkT)}{\partial C_n} = 0 \tag{11}$$

for all C_n. Differentiation of Eq. (8) yields [6]

$$-\beta + \alpha - 2C_n\alpha + \ln(C_n - C_{n+1}) - \ln(C_{n-1} - C_n) = 0 \,, \tag{12}$$

which must be solved numerically.

3. KINETIC ZEROTH-ORDER MODEL

3.1. Single-layer model

Recently, a simple kinetic single-layer model was proposed in Ref. [11]. In contrast to the kinetic MC simulations, where full information about the location of each unit in the lattice is used, the model is based on zeroth-order approach and the state of the interface layer is described by the fraction $C = N_s/N$ of solid cells. Among the N sites in the layer, creations are possible only in $N(1–C)$ cells filled with fluid and the average frequency k_i^+ of creation in a given fluid site depends on the number i of its nearest lateral solid neighbours. Similarly, annihilations are limited to NC sites filled with solid blocks and the average frequency k_i^- also depends on the number i of solid neighbours. Considering the change dC during time dt as the consequence of the difference between the flux of molecules being created and the annihilation flux, we can easily write equation describing the time evolution of the boundary layer [11]

$$dC = \left[(1-C)\sum_{i=0}^{4} p_i k_i^+ - C\sum_{i=0}^{4} p_i k_i^- \right] dt\,, \tag{13}$$

where p_i is the probability of finding exactly i lateral neighbours around a particular location in the interface layer. In the zeroth-order approach the probability of finding a solid block at any single location is always C, regardless of the type of blocks in the neighbourhood. Hence, the probability p_i is given by Bernoulli trial

$$p_i = \binom{4}{i} C^i (1-C)^{4-i}\,. \tag{14}$$

The rate constants k_i^+ and k_i^- result from the Arrhenius equation

$$k = k_0 \exp(-E_a / kT)\,, \tag{15}$$

where k_0 is the number of trials to occur per unit time and E_a is the activation free energy. According to the Binsbergen’s model of nucleation, a jump from one free energy level $\Delta G_{j–1}$ to the next level $\Delta G_{j–1}$ is hampered by a free energy of activation of viscous flow or of rotational diffusion ΔG_η and the total free energy of activation is given by [10]

$$E_a = \Delta G_\eta + \tfrac{1}{2}(\Delta G_j - \Delta G_{j-1})\,. \tag{16}$$

In the equilibrium state ($\beta = 0$) the energies ΔG_j and ΔG_{j-1} result from consideration of changes in the number of solid-solid, fluid-fluid, and solid-fluid bonds. If the effect of supersaturation is also taken into account, the following rate constants are finally obtained [7, 10]

$$k_i^+ = f_t \cdot \exp[-\alpha(2-i)/4 + \beta/2], \tag{17}$$

$$k_i^- = f_t \cdot \exp[\alpha(2-i)/4 - \beta/2], \tag{18}$$

where f_t is a constant with dimension of reciprocal time

$$f_t = \frac{kT}{h}\exp\left(-\frac{\Delta G_\eta}{kT}\right). \tag{19}$$

3.2. New multilayer kinetic model

Let us now consider a kinetic zeroth-order model which does not limit the numbers of layers in the interface region. The model proposed in this work is based on simple statistics similar to that presented in Section 3.1. The state of the crystal-mother-phase interface will be described in a way known from the Temkin thermodynamic model, i.e. by the array of fractions C_n, where the number n of layer varies from $-\infty$ to $+\infty$. Moreover, we follow the boundary conditions $C_{-\infty} = 1$ and $C_{+\infty} = 0$ as well as solid-on-solid assumption which leads to $C_{n+1} \le C_n$.

Considering the creations, we must take into account that, among $N(1 - C_n)$ fluid blocks in the n-th layer, $N(1 - C_{n-1})$ blocks have no solid neighbours in the $(n - 1)$-th layer. Thus, the number of sites available for creation that satisfy solid-on-solid assumption is $N(C_{n-1} - C_n)$. Similarly, among NC_n solid blocks in the n-th layer, NC_{n+1} of them have a solid neighbour in the $(n + 1)$-th layer, which implies that the number of sites available for annihilations is $N(C_n - C_{n+1})$. Thus, Eq. (13) generalized for any n-th layer in a multilayer interface takes the form

$$dC_n = \left[(C_{n-1} - C_n)\sum_{i=0}^{4} p_{n,i}\, k_i^+ - (C_n - C_{n+1})\sum_{i=0}^{4} p_{n,i}\, k_i^-\right] dt\,, \tag{20}$$

where the probability $p_{n,i}$ of finding exactly i lateral neighbours around a particular location in the n-th layer is given by

$$p_{n,i}=\begin{cases}0, & \text{for } (C_n=0 \text{ and } i\neq 0) \text{ or } (C_n=1 \text{ and } i\neq 4),\\ \binom{4}{i}C_n^i\left(1-C_n\right)^{4-i}, & \text{for } C_n\neq 0 \text{ and } C_n\neq 1,\\ 1, & \text{for } (C_n=0 \text{ and } i=0) \text{ or } (C_n=1 \text{ and } i=4).\end{cases} \tag{21}$$

It is convenient to start the calculations at $t = 0$ from a perfectly flat boundary between completely solid and completely fluid layers, i.e. $C_n = 1$ for $n \leq 0$ and $C_n = 0$ for $n > 0$. Therefore, the special cases in Eq. (21) for $C_n = 0$ and $C_n = 1$ are necessary to avoid indefinite symbol 0^0.

The multilayer kinetic model described above allows for direct comparison of the results with the results of the thermodynamic Temkin model. This comparison can be considered as a compliance test between kinetic and thermodynamic approaches, while the other assumptions made are as close as possible. Moreover, thanks to a well-defined time t in the crystal-mother-phase system, the kinetic model allows to calculate the average growth rate R of crystal face

$$R=\frac{d\sum_{n=-\infty}^{n=+\infty}[C_n(t_2)-C_n(t_1)]}{t_2-t_1}, \tag{22}$$

where d is the thickness of one layer of growth units. Of course, comparison of the rate R with the results of Temkin model is not possible. However, it is interesting to make a comparison with the results of MC simulations.

4. RESULTS AND DISCUSION

The Temkin thermodynamic model leads to a system of equations (12). Numerical solution of this system of equations shows that a true minimum of $\Delta G(C_n)$ and not a saddle point may exist or not depending on the values of α and β parameters. As shown in Fig. 1, a critical value α_c is about 1.07 at equilibrium state ($\beta = 0$) and this value increases with increasing β. In the case $\beta = 0$ no growth is possible and α_c is traditionally related to the roughening temperature $T^R = 4\phi/k\alpha_c$, i.e. if $\alpha > \alpha_c$ or $T < T^R$ the solid and fluid fractions are separated, and if $\alpha < \alpha_c$ or $T > T^R$ a mixture of solid and fluid blocks become one phase. In the nonequilibrium state (i.e. $\beta > 0$) there are no thermodynamic barriers for crystal growth in the field B in Fig. 1 and the crystal grows continuously, whereas if growth occurs in the A field only a layer growth is possible (by a two-dimensional nucleation mechanism or a spiral growth mechanism) [6].

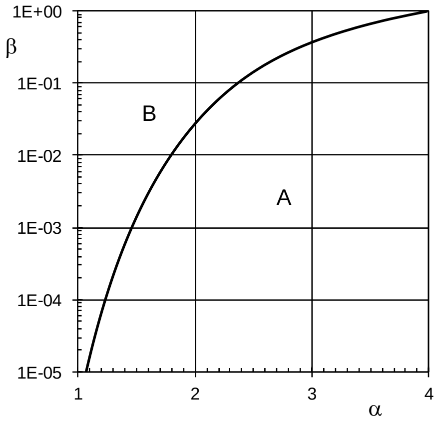

Fig. 1. Curve resulting from the Temkin thermodynamic model which separates the area A where the Gibbs free energy ΔG has a minimum for each C_n and the area B where there is no minimum of ΔG

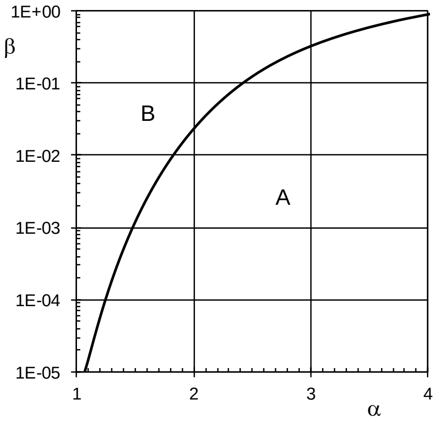

Fig. 2. Curve resulting from the kinetic zeroth-order multilayer model which separates the area A where $C_n(t)$ dependencies tend to a steady state and area B where there are no limits to the evolution of $C_n(t)$

When the kinetic model proposed in section 3.2 is considered, we cannot investigate the existence of a minimum of $\Delta G(C_n)$, but we can check whether the $C_n(t)$ dependencies resulting from numerical solution of Eq. (20) tend to a steady state after a sufficiently long time, or are changing all the time. The results obtained in this way and shown in Fig. 2 appear to be very similar to those in Fig. 1 which result from the Temkin model. As the both models do not limit the number of layers in the interface, we had to impose an additional limit of 30 layers while solving Eqs. (12) and (20) numerically.

The Temkin model was also used to find the profiles of concentration of solid blocks in the interface layers [6]. Profiles of this type may also be easily obtained on the basis of the kinetic model proposed in section 3.2. As shown in Figs. 3 and 4, some exemplary profiles obtained for $\beta = 0$ using Temkin and kinetic models are almost indistinguishable. However, a full comparison of the both models for any values of the α and β parameters is not possible. This limitation results from the nature of the thermodynamic approach, which allows us to find a solution only when the steady state is reached. This problem does not appear in the kinetic model where the time evolution of the system may be considered for any arbitrary conditions.

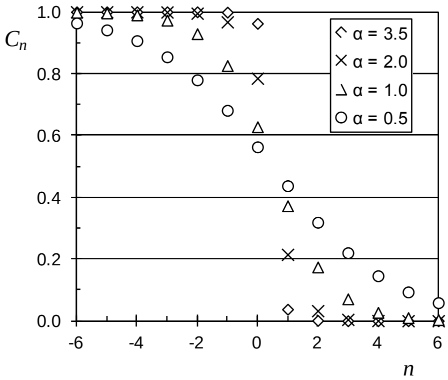

Fig. 3. Profiles of concentration of solid blocks C_n resulting from the Temkin thermodynamic model for the equilibrium state (β = 0) and selected values of α

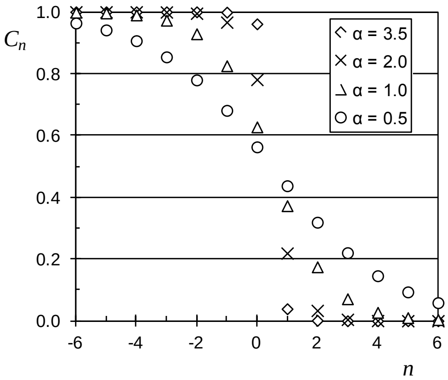

Fig. 4. Profiles of concentration of solid blocks C_n resulting from the kinetic zeroth-order multilayer model for the equilibrium state (β = 0) and selected values of α

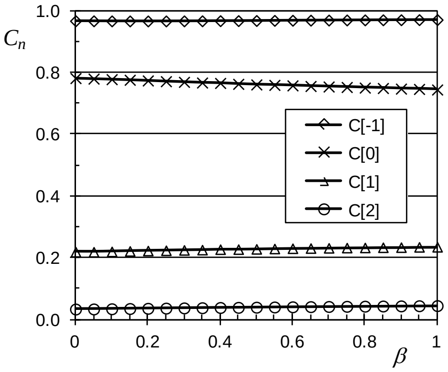

Fig. 5. Influence of β parameter on the profile of concentration of solid blocks C_n resulting from kinetic zeroth-order multilayer model calculated for α = 2

Figure 1 shows that, if we start from the point in the field A, the field B may be achieved by reducing the value of α or by increasing the value of β. In both cases the surface will be roughened, but the reasons are different. In the former case it is high temperature whereas in the second case it is a high driving force for the crystallization. As the Temkin, Mutaftschiev and Jackson thermodynamic models do not offer any other possibilities for studying these two roughening mechanisms, it may be concluded that the effect achieved is the same in both cases [2]. However, the profile of concentration of solid blocks resulting from our kinetic model and presented in Figure 5 show, that the β parameter has a very weak effect on the profile, while the impact of α is crucial (see Fig. 4).

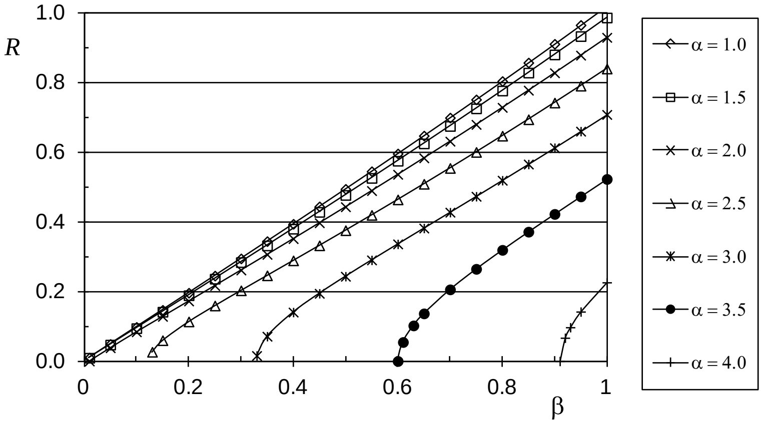

Fig. 6. Dependence of average growth rate *R* on the β parameter resulting from the kinetic model described in section 3.2 for selected values of α

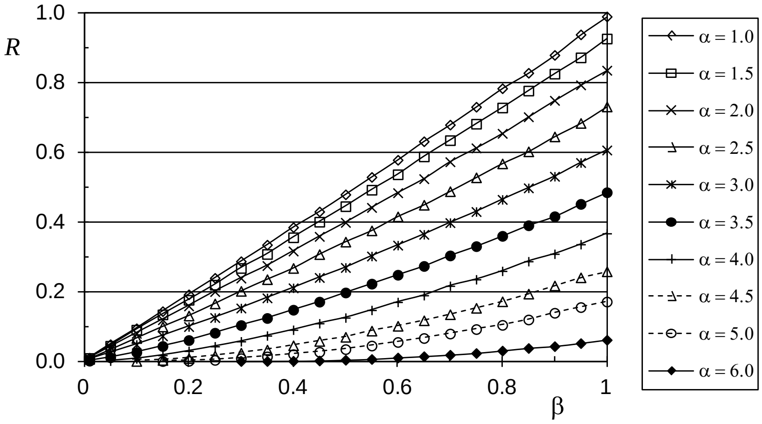

Fig. 7. Dependence of average growth rate *R* on the β parameter resulting from kinetic Monte Carlo simulations performed for the surface array 60 × 60 and no surface diffusion for selected values of α

In order to examine the impact of the zeroth-order approximation, the average growth rates resulting from our kinetic model and Eq. (22) were compared with analogous rates obtained from kinetic MC simulations using simulation algorithm described in Ref. [9]. The results qualitatively consistent with our dependencies shown in Fig. 7 were also obtained by other authors (see, e.g., Refs. [14, 15]). As the same formulae (17) and (18) for the frequencies of creation and annihilation were used in both compared models, the only significant difference was the use of zeroth-order approximation in our kinetic model and an array containing information about the locations of solid and fluid blocks in MC simulations. The results presented in Figs 6 and 7 show that both methods lead to similar growth rates only for $\alpha \leq 2.0$, but substantially different shapes of $R(\beta)$ dependencies are visible for $\alpha \geq 2.5$. Furthermore, the rapid fall to zero of the values of R predicted by our kinetic zeroth-order model for $\alpha \geq 2.5$ seems to be inconsistent with experimental data. These results show that the zeroth-order approximation is very rough and preferential clustering must be taken into account in further research.

5. CONCLUSIONS

A simple kinetic block model of multilayer crystal-mother-phase interface is proposed in this work. The model uses Bragg-Williams approximation, "solid-on-solid" assumption and the state of the interface is described by an array of concentrations of solid blocks in individual layers within the interface. Our kinetic model leads to the results which are very similar to those obtained previously by the thermodynamic Temkin model. This comparison shows that kinetic and thermodynamic approaches are substantially equivalent when there are no other significant differences between models. Thus, the differences between findings from the Temkin model and kinetic MC simulations, which were reported earlier in the literature, result from other assumptions rather than those from different thermodynamic and kinetic approaches.

Our kinetic model includes both the steady-state case and the case of an unlimited time evolution of the system. The latter case is not covered by the thermodynamic models, where the time in the crystal-mother-phase is not defined. The growth rates of crystal face obtained using our kinetic zeroth-order model differ significantly from the results of kinetic MC simulations, where long-range ordering is taken into account. This comparison shows that the zeroth-order approximation turns out to be the main problem of all zero-order kinetic and thermodynamic models. It will be shown in a forthcoming paper [12] that preference for bonds between blocks of the same type over mixed-type bonds may easily be introduced into our kinetic model.

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ANALITYCZNY KINETYCZNY MODEL BLOKOWY WIELOWARSTWOWEJ GRANICY FAZ KRYSZTAŁ-FAZA MACIERZYSTA

Streszczenie

Zaproponowano prosty kinetyczny blokowy model wielowarstwowej granicy faz kryształ-faza macierzysta. Model ten prowadzi do układu równań różniczkowych, które rozwiązuje się bez potrzeby przeprowadzania symulacji Monte Carlo. Zaproponowany model wykorzystuje przybliżenie Bragga-Williamsa (zwane także przybliżeniem zerowego rzędu), założenie znane w literaturze jako „solid-on-solid" oraz inne założenia wspólne z termodynamicznym modelem Temkina, co umożliwia sprawdzenie zgodności podejścia kinetycznego i termodynamicznego w sytuacji gdy nie występują inne istotne różnice pomiędzy modelami. Ponadto porównanie zaproponowanego modelu z kinetycznymi symulacjami Monte Carlo umożliwia lepsze zrozumienie znaczenia przybliżenia Bragga-Williamsa.