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MODIFICATION OF BRAGG-WILLIAMS APPROXIMATION APPLIED IN JACKSON'S MODEL OF CRYSTAL GROWTH

Results of Monte Carlo simulations for single-layer solid-fluid interface were compared with Bragg-Williams approximation, which describes the number of bonds between solid and fluid cells in Jackson's crystal growth model. The comparison shows that Bragg-Williams approximation produces much higher values than those resulting from simulations. The use of better approximations based on the results of the simulation does not lead directly to improvement of predictions given by Jackson's model, but rather reveals further problems. In particular, the estimation of entropy seems to be also very overvalued. Monte Carlo simulations were used also to investigate the number of stable states of a single boundary layer for various crystal growth conditions. The results obtained differ significantly from those resulting from the analysis of free energy minima in Jackson's model, but are in good agreement with the results of multi-layer simulations.

Keywords: Bragg-Williams approximation, Jackson's model of crystal growth, Monte-Carlo simulations.

1. INTRODUCTION

1.1. Motivation and aim of the paper

Jackson's one-layer model describes the crystal-mother phase interface using very simple statistics and provides the results concerning crystal growth mechanisms. Although its serious limitations are known (see e.g. [1]) and many years have passed since the first publication in 1958 [2], the model is still interesting because of its didactic importance: it is relatively easy to understand, illustrates a number of essential concepts for the science of crystal growth, and

allows to derive an analytical solution. The model has been extended by Mutaftschiev [3] for two-layers interface and later generalized by Temkin [4,5] to multi-layers model. Allowing a thicker interface influenced the results noticeably, but this was achieved at the cost of more difficult solving of the obtained equations. Meanwhile, a number of other rough approximations remain in all of these models and they are suspected of spoiling the final results. For this reason, confrontation with studies based on computer simulations does not show satisfactory compliance.

The main purpose of this work is to improve the Bragg-Williams approximation employing Monte Carlo simulations of crystal growth. Due to the simplicity of Jackson's model we focused in this work on the case of single-layer interface. Bragg-Williams approximation describes the total average number N_{sf} of solid-fluid bonds between closest-neighboring units

$$N_{sf} = z \, x_s \, (1 - x_s), \tag{1}$$

where z is the number of the closest neighboring cells and $x_s = N_s/N$ is the fraction of solid cells in the interface layer, i.e. the ratio of the number of solid cells N_s to the number of all cells N. Since solid on solid (SOS) assumption is applicable in Jackson's model, only lateral neighbors are taken into account. Typically the cubic and tetragonal crystals are considered and $z = 4$.

The Bragg-Williams approximation is based on the assumption of ideally random mixing of solid and liquid cells. Such an assumption is justified in the case of gas mixture, whereas for the crystal-mother phase interface it seems to contradict well known crystal growth mechanisms, e.g. growth by two-dimensional nucleation. Any form of grouping of one type cells leads to a reduction in the number of solid-fluid bonds N_{sf} in comparison to a random mixture. The great advantage of Monte Carlo simulation is the lack of any assumptions about the ordering of elementary units.

An additional goal of this work is to find stable states of single-layer solid-fluid interface for various growth conditions on the basis of the evolution of the interface during Monte Carlo simulation. The results of such analysis are confronted with the analysis of free energy minima known from the Jackson's approach. This approach should reduce the methodological differences between Jackson's thermodynamic model and Monte Carlo simulations.

1.2. Jackson's model

Jackson's model of crystal-mother phase interface was described step by step in some previous papers [1,2]. Here we recall only briefly some selected fragments, which are important for understanding of this work. We also tried to correct some minor editorial mistakes, which were found in the formulas given in [1].

The conditions of crystal growth in Jackson's model are described by two coefficients: the Temkin coefficient α and the coefficient β related to kinetic roughening. The Temkin coefficient is defined as

$$\alpha = \frac{z\,\Phi}{kT}\,, \qquad (2)$$

where $z = 4$ for the assumed cubic or tetragonal crystal, k is the Boltzmann constant, T is the temperature, and Φ is a change in bond energy when a solid cell in a pure solid crystal and a fluid cell in a pure fluid area are exchanged

$$\Phi = \Phi^{sf} - \frac{1}{2}(\Phi^{ss} + \Phi^{ff})\,. \qquad (3)$$

The symbols Φ^{sf}, Φ^{ss} and Φ^{ff} denote negative energies related to solid-fluid, solid-solid, and fluid-fluid bonds, respectively.

The second parameter β describes the driving force of crystallization

$$\beta = \frac{\mu_f - \mu_s}{kT} = \ln(1 + \sigma)\,, \qquad (4)$$

where μ_f and μ_s are the standard chemical potentials of the fluid and liquid cells, respectively, and σ is relative supersaturation of mother phase.

In Jackson's thermodynamic model a two-dimensional 100% solid crystal and a 100% fluid area was taken as a reference state. The free energy F^r of this reference system depends on the number N_s of solid cells and the number N_f of fluid cells

$$F^r = \mu_s N_s + \mu_f N_f\,. \qquad (5)$$

The change of free energy due to the mixing of solid and fluid cells is given by

$$\Delta F_{mix} = \Delta U_{mix} - T\,\Delta S_{mix}\,, \qquad (6)$$

where ΔU_{mix} and ΔS_{mix} are the energy of mixing and the entropy of mixing, respectively. Total change of free energy is

$$\Delta F = F^r + \Delta F_{mix}\,. \qquad (7)$$

The energy ΔU_{mix} in Eq. (6) depends on estimation of the number N_{sf} of solid-fluid bonds in the mixture

$$\Delta U_{mix} = NKT\alpha N_{sf}\,. \qquad (8)$$

Assuming random mixing of the blocks, Bragg-Williams approximation given by the formula (1) may be substituted into Eq. (8). The entropy ΔS_{mix} in Eq. (6) is given by Boltzmann expression

$$\Delta S_{mix} = k\ln(g). \qquad (9)$$

where g is the number of configurations of the system under consideration. All possible states are treated as equally probable. For the reference state $g = 1$ and after mixing

$$g = \frac{N!}{N_s! N_f!}. \tag{10}$$

After some transformations the following formula can be derived:

$$f(x_s) = \frac{\Delta F}{NkT} = \alpha x_s(1-x_s) + x_s \ln x_s + (1-x_s)\ln(1-x_s) - \beta x_s. \tag{11}$$

The function $f(x)$ has one or two minima depending on the crystal growth conditions given by the α and β parameters (see e.g. Fig. 1). In the case of thermodynamic equilibrium state $\beta = 0$ the function (11) has only one minimum for $x_s = 0.5$ when $\alpha < 2$ and two minima for x_s close to 0 and 1 when $\alpha > 2$. It means that one phase consisting of 50% solid cells mixed with 50% fluid cells is stable when $\alpha < 2$, and large nearly solid domains separated by nearly fluid regions are stable when $\alpha > 2$. The critical value α^c of α for supersaturated mother phase ($\beta > 0$) is higher than 2 and increases with increasing value of β.
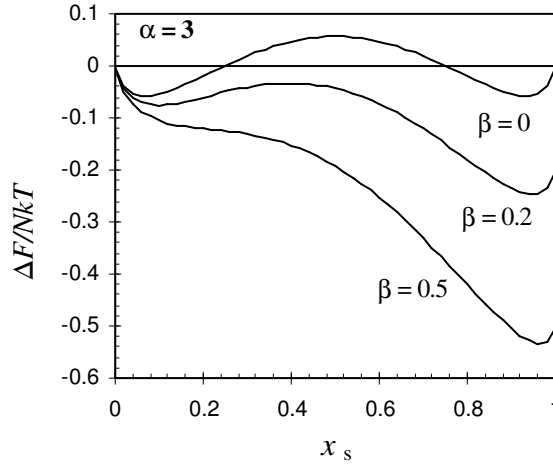

Fig. 1. Relative free energy $\Delta F/NkT$ described by the formula (11) as a function of the fraction x_s of solid cells in the interface, plotted for Temkin coefficient $\alpha = 3$ taken as an example, and various values of parameter β

2. MONTE CARLO SIMULATIONS

2.1. Simulation algorithm

Our Monte Carlo simulations are based on the algorithm known from the early papers of Gilmer and Bennema [6,7]. In order to adopt this

algorithm to the specific properties of Jackson's model the following modifications were made:
1) Surface diffusion was omitted, i.e., the length of diffusion path $X_s = 0$.
2) Solid-fluid interface was limited to one layer of growth units. In contrast to multi-layer simulations, it is necessary to introduce an additional lock for these creations and annihilations, which cannot be performed inside fixed boundary layer for given (x, y) coordinates. According to solid on solid (SOS) assumption all layers below the single-layer interface are always completely filled with solid blocks and all layers above the interface are filled with only fluid blocks.

In our simulations the solid-fluid interface was described by an array of 200×200 growth units. This size was chosen as a compromise between the time necessary to carry out our numerous simulations and the reliability of the obtained results [8].

2.2. Methods for analysis of simulation results

The results of performed single-layer Monte Carlo simulations were used to obtain the following data:
1) Changing the interface state during the simulation enabled calculation of the average number of solid-fluid bonds N_{sf} as a function of the fraction x_s of solid blocks. In order to reduce fluctuations of the results, each forward and backward crossing through each of 200 selected values of x_s was registered.
2) During the simulation run for a sufficiently long time, single-layer interface reaches steady state, and only small fluctuations around the average stable value of x_s are recorded. We concluded from the observations that the number of possible stable values of x_s is one or two and it depends on the conditions of crystal growth. The results presented in such form have two useful features: (a) the analogy to the analysis of free energy minima in Jackson's model is clearly visible, (b) the transition between one and two stable values of x_s is sharp for small changes in growth conditions.

The simulation was carried out at least twice for each set of α and β parameters, applying different initial conditions: $x_{s,init} = 0$ (completely liquid interface) and $x_{s,init} = 1$ (completely solid interface). When existence of two considerably different stable values of x_s was detected, numerous additional simulations were performed, starting with purely random mixture of solid and fluid growth units in the interface for $x_{s,init} = 0.5$. The results obtained during rapid grouping of units of the same type for x_s oscillating near 0.5 were omitted from our diagrams.

2.3. Frequencies of creation and annihilation

The results presented in this paper relate to the crystal growing from solution. According to the formulae derived by Binsbergen the frequencies of creation k_i^+ and annihilation k_i^- are [9]:

$$k_i^+ = f_t \cdot \exp\left[-\frac{\alpha}{4}(i-2)+\frac{\beta}{2}\right], \qquad (12)$$

$$k_i^- = f_t \cdot \exp\left[\frac{\alpha}{4}(i-2)-\frac{\beta}{2}\right]. \qquad (13)$$

The frequency f_t is

$$f_t = \frac{kT}{h}\exp\left(-\frac{\Delta G_\eta}{kT}\right), \qquad (14)$$

where ΔG_η is a free energy of activation of viscous flow or of rotational diffusion.

In the case of the growth from vapour different formulas should be used, which are given e.g. in Refs. [6,7]. Application of these formulas, however, leads to very similar results.

3. RESULTS

3.1. Thermodynamic equilibrium state

We will start by considering a state of thermodynamic equilibrium, which corresponds to $\beta = 0$. The results of our Monte Carlo simulations show that Bragg-Williams approximation given by formula (1) is quite good only when α is close to zero. This approximation becomes more and more overvalued with increasing values of α for a wide range of x_s (Fig. 2). Monte Carlo simulations and formula (1) give similar results only for the interface layer almost completely filled with blocks of the same type. The dependencies N_{sf}/N on x_s obtained using both these approaches have the diagonal asymptote $N_{sf}/N = 4x_s$ for $x_s \rightarrow 0$ and the asymptote $N_{sf}/N = 4(1 - x_s)$ for $x_s \rightarrow 1$.

The results of Monte Carlo simulation suggest that the following empirical formula can be proposed instead of the Bragg-Williams approximation:

$$\frac{N_{sf}}{N} = \frac{4}{S}\left[1 - e^{Sx_s(x_s-1)}\right],\tag{15}$$

where S is an empirical parameter depending on Temkin coefficient α. The plots of the function (15) for various values of α with values of S adjusted for best fit to simulation results are shown in Fig. 2. The function reaches its maximum for $x_s = 0.5$

$$\left(\frac{N_{sf}}{N}\right)_{max} = \frac{4}{S}\left(1 - e^{-S/4}\right).\tag{16}$$

Equilibrium state ($\beta=0$)

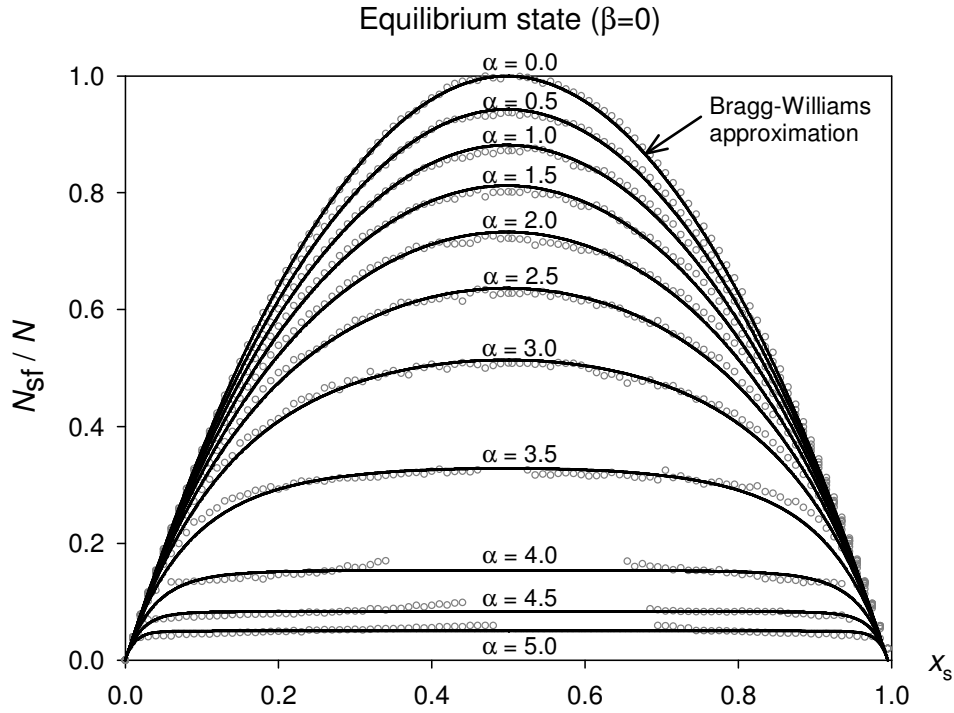

Fig. 2. Average number N_{sf} of solid-fluid bonds to the number N of cells as a function of the fraction x_s of solid cells in the interface layer plotted for $\beta = 0$. Circles show the results of individual Monte Carlo simulations, solid lines are plotted according to the function given by the formula (15)

The results of simulations show that the $S(\alpha)$ dependence is a nearly linear function $S = \alpha$ for α close to zero and tends to another linear relationship with a

much larger slope coefficient A for large values of α. These observations allow us to propose an empirical formula:

$$S(\alpha) = \alpha + \frac{A-1}{B}\ln\left[e^{B(\alpha-C)} + 1\right],\tag{17}$$

where $A = 199.40$, $B = 1.8947$, $C = 4.8157$ are dimensionless constants. The values of these constants were calculated by least-squares method for the smallest difference between the values of $(N_{sf}/N)_{max}$ resulting from Monte Carlo simulations and the approximation $(N_{sf}/N)_{max} = f(S(\alpha))$ obtained by substitution of Eq. (17) into (16). The results of simulations and their approximation are shown in Fig. 3.
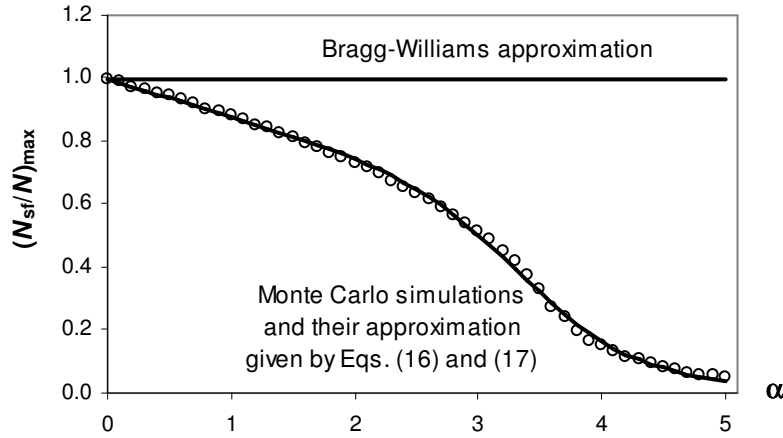

Fig. 3. Maximum values of the N_{sf}/N ratio for $x_s = 0.5$ obtained from Bragg-Williams approximation (1) and Monte Carlo simulations carried out for $\beta = 0$. Circles show the results of individual Monte Carlo simulations for various values of α, solid line represents the approximation obtained by substitution of Eq. (17) into (16)

In the case of $\alpha = 0$ the approximation given by formula (15) becomes very close to Bragg-Williams approximation (1). The exact equality of these two approximations would come for $S = 0$

$$\lim_{S \to 0} \frac{4}{S}\left[1 - e^{Sx_s(x_s-1)}\right] = 4x_s(1 - x_s).\tag{18}$$

However, because of the approximate nature of Eq. (17) we obtain $S \approx 0.0114$ for $\alpha = 0$, which corresponds to $(N_{sf}/N)_{max} \approx 0.9986$ according to Eq. (16).

3.2. Kinetic roughening

Crystal surface can become rough due to two main reasons: (a) temperature and (b) the supersaturation of the mother phase, which leads to crystallization. The existence of a driving force for crystallization ($\beta > 0$) should therefore increase the number of solid-fluid bonds N_{sf} in comparison to the equilibrium state discussed in previous chapter. This effect, called kinetic roughening, becomes visible when the temperature roughening gradually loses importance with increasing Temkin coefficient α (see Fig. 4). Moreover, kinetic roughening has the greatest importance for the values of x far from 0 (fully fluid layer) and 1 (fully solid layer). It should be pointed out, however, that this state becomes more and more unstable with increasing values of the α and β coefficients.
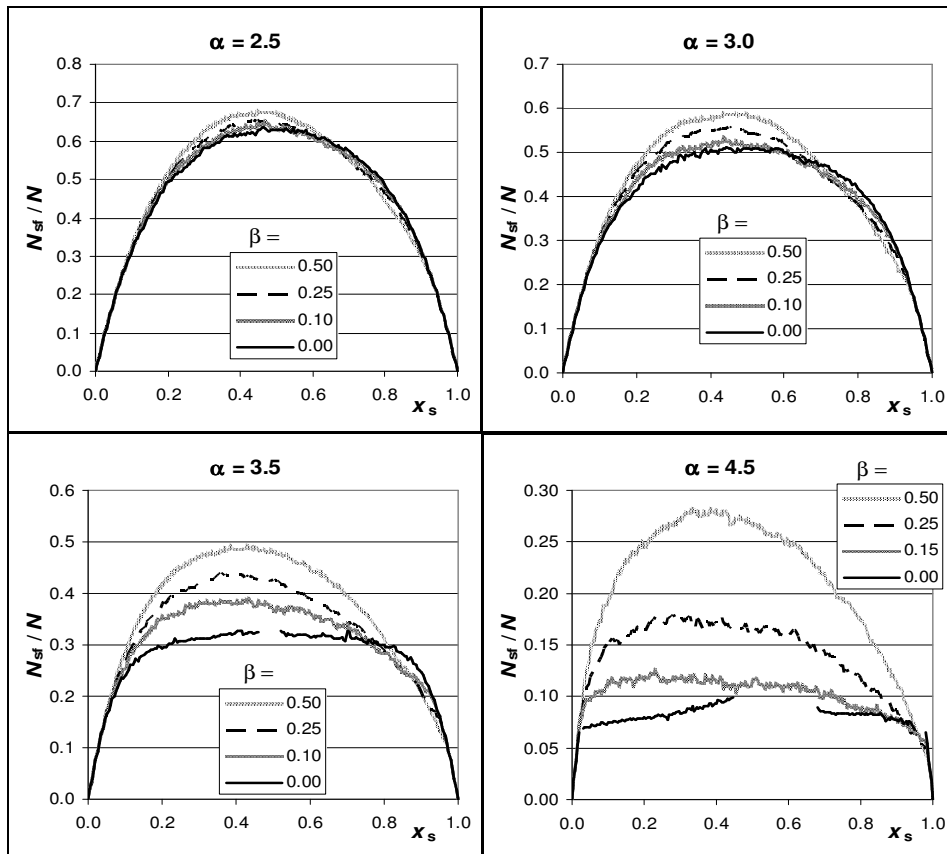

Fig. 4. Average number N_{sf} of solid-fluid bonds to the number N of cells as a function of the fraction x_s of solid cells in the interface layer plotted for various values of β

3.3. Stable states of solid-fluid interface

The results of our Monte Carlo simulations indicate that single-layer interface does not affect noticeably the estimation of the critical value α^c of Temkin coefficient α for the transition between the continuous and layered growth mechanism. The transition between one and two possible stable values of x_s (fraction of solid blocks in the interface) was observed for $\alpha^c \approx 3.4$ in thermodynamic equilibrium state $\beta = 0$. This result is consistent with a value of 3.2…3.5 estimated on the basis of crystal surface roughening observed in multi-layer simulations for β close to 0.

4. DISCUSSION

The kinetic roughening phenomena considered in Section 3.2 manifest themselves most clearly in conditions which are also the most unstable. Thus, the approximation of $N_{sf}(x_s)$ dependence proposed in Section 3.1 for $\beta = 0$ seems to be acceptable also for $\beta > 0$. Such an approximation is slightly underestimated, but it is certainly better than highly overestimated Bragg-Williams approximation.

Jackson's model of the crystal-mother phase interface leads to estimation of free energy in the form given by formula (11). Replacing only the Bragg-Williams approximation with the approximation based on the results of Monte Carlo simulations causes a radical change in estimation of free energy

$$\frac{\Delta F}{NkT} = \frac{\alpha}{S}\left[1 - e^{Sx_s(x_s - 1)}\right] + x_s \ln x_s + (1 - x_s)\ln(1 - x_s) - \beta x_s, \qquad (19)$$

where the dependence of the S parameter on Temkin coefficient α is described by Eq. (17). After making this change the free energy given by the formula (19) has only one minimum (for $x_s = 0.5$ in the equilibrium state $\beta = 0$) irrespective of the value of α. Unfortunately, this result indicates that the model completely stopped working! Such a negative result does not imply, however, that the results provided by Monte Carlo simulations are definitely wrong. We believe rather that the reliability of other components included in the calculation of free energy in the Jackson's model is also questionable. The impression that the model in its original form works more or less correctly is the result of cumulative effects of several very rough approximations. In particular, the entropy calculated using the Boltzmann expression (9) seems to be highly overvalued. The various possible configurations of solid and liquid blocks in the interface layer can vary significantly in terms of their likelihood. For this reason,

estimation of entropy is a task much more complicated than in the Boltzmann's approach and needs some further works.

According to the results of our single-layer Monte Carlo simulations the transition between one and two possible stable values of x_s was observed for $\alpha^c \approx 3.4$ in thermodynamic equilibrium state $\beta = 0$. This result is consistent with multi-layer Monte Carlo simulations, but predictions based on the original Jackson's model differ significantly – the transition between one and two minima of the function $\Delta F(x_s)$ given by the formula (11) occurs for $\alpha^c = 2.0$. We are convinced that the main reason of this discrepancy is the assumption of purely random mixing of solid and liquid cells in the interface used in Jackson's model. This assumption underlies Bragg-Williams approximation as well as Boltzmann expression describing the entropy.

6. CONCLUSIONS

The assumption of a single-layer crystal-mother phase interface applied in Jackson's model does not seem to cause significant error. This assumption is very beneficial to simplify the analysis of the formulas obtained. However, there is also a number of other very rough approximations, which are common to single-layer Jackson's model and multi-layer Temkin's model. In this paper we proposed to replace Bragg-Williams approximation by an approximation based on the results of Monte Carlo simulations, in which the formation of groups of solid blocks is taken into account. Differences between the proposed approximation and the Bragg-Williams approximation clearly increase with increasing value of Temkin coefficient. Introducing just this one improvement in Jackson's model did not lead to satisfactory results but further problems have become more visible. In particular, the next problem that should be considered is a more realistic estimation of the entropy.

ACKNOWLEDGEMENTS

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MODYFIKACJA PRZYBLIŻENIA BRAGGA-WILLIAMSA W MODELU JACKSONA WZROSTU KRYSZTAŁÓW

Streszczenie

Wyniki symulacji Monte Carlo dla jednowarstwowej granicy faz porównano z przybliżeniem Bragga-Williamsa, które w modelu Jacksona wzrostu kryształów opisuje liczbę wiązań między blokami stałymi i ciekłymi. Porównanie to pokazało, że przybliżenie Bragga-Williamsa daje znacznie większe wartości od tych otrzymanych na podstawie symulacji. Zastosowanie lepszego przybliżenia opartego na wynikach symulacji nie prowadzi wprost do poprawy przewidywań modelu Jacksona, lecz raczej ujawnia kolejne problemy. W szczególności oszacowanie entropii wydaje się także bardzo zawyżone.

Symulacje Monte Carlo zastosowano także do zbadania liczby stanów stabilnych pojedynczej warstwy granicznej w zależności od warunków wzrostu kryształu. Uzyskane wyniki różnią się znacznie od tych wynikających z analizy liczby minimów energii swobodnej w modelu Jacksona, natomiast pozostają w dobrej zgodności z wynikami symulacji wielowarstwowych.