

INHOMOGENEOUS DISLOCATION STRUCTURES OF DISCLINATED GRAIN BOUNDARIES IN GRAPHENE AND ULTRAFINE-GRAINED METALS

Ya.V. Konakov^{1,2}, I.A. Ovid'ko^{1,2,3} and A.G. Sheinerman^{1,2}

¹ Department of Mathematics and Mechanics, St. Petersburg State University, Universitetskii pr. 28, Staryi Peterhof, St. Petersburg 198504, Russia

² Institute of Problems of Mechanical Engineering, Russian Academy of Sciences, Bolshoj 61, Vasil. Ostrov, St. Petersburg 199178, Russia

³ St. Petersburg State Polytechnical University, St. Petersburg 195251, Russia

Received: November 1, 2013

Abstract. A theoretical model is suggested which describes distribution of grain boundary (GB) dislocations at GBs initially containing partial (non-topological) disclinations in polycrystalline graphene and ultrafine-grained metals. Such partial disclinations at GBs are associated with experimentally observed structural irregularities of real GBs in graphene and metals. Within the suggested model, spatial distribution of GB dislocations – basic structural units of GBs – are theoretically revealed as those depending on GB misorientation parameters and characteristics (strength, spatial location) of pre-existent GB disclinations in polycrystalline graphene and ultrafine-grained metals.

1. INTRODUCTION

Graphene and ultrafine-grained metals represent advanced materials with unique mechanical and functional properties; see, e.g., [1-10]. In particular, graphene exhibits the outstanding mechanical and transport properties which are sensitive to its structural features and geometry [2-5]. Recently, large-area graphene sheets with polycrystalline structures have become the subject of intense research efforts; see, e.g., [11-14]. GBs serve as intrinsic structural elements in such polycrystalline graphene sheets and strongly influence their mechanical and functional characteristics; see reviews [15,16]. Also, ultrafine-grained metals are specified by large amounts of GBs which crucially affect mechanical and physical properties of these metals [6-10]. In both polycrystalline graphene and ultrafine-grained metals in their as-fabricated states,

GBs typically have rather irregular structures with misorientation parameters that may vary along GBs [6-9,15,16]. For instance, the experimentally observed [17,18] irregularities in real GB structures in graphene often violate both their strict periodicity and thereby ideal constancy of the GB misorientation along GB lines. Within the approach presented in papers [15,19,20], partial GB disclinations are viewed as GB defects associated with elementary changes in the GB misorientation in graphene. Such partial disclinations in two-dimensional (2D) graphene sheet represent GB points where GB misorientation changes in a step-like manner (and so does the GB dislocation arrangement; see, e.g., Figs. 1a and 1b) [15,19,20]. More precisely, by analogy with partial wedge disclinations at 2D GBs in conventional three-dimensional (3D) solids [21-24], a partial disclination at a line GB in graphene is defined as a point

Corresponding author: I.A. Ovid'ko, e-mail: ovidko@nano.ipme.ru

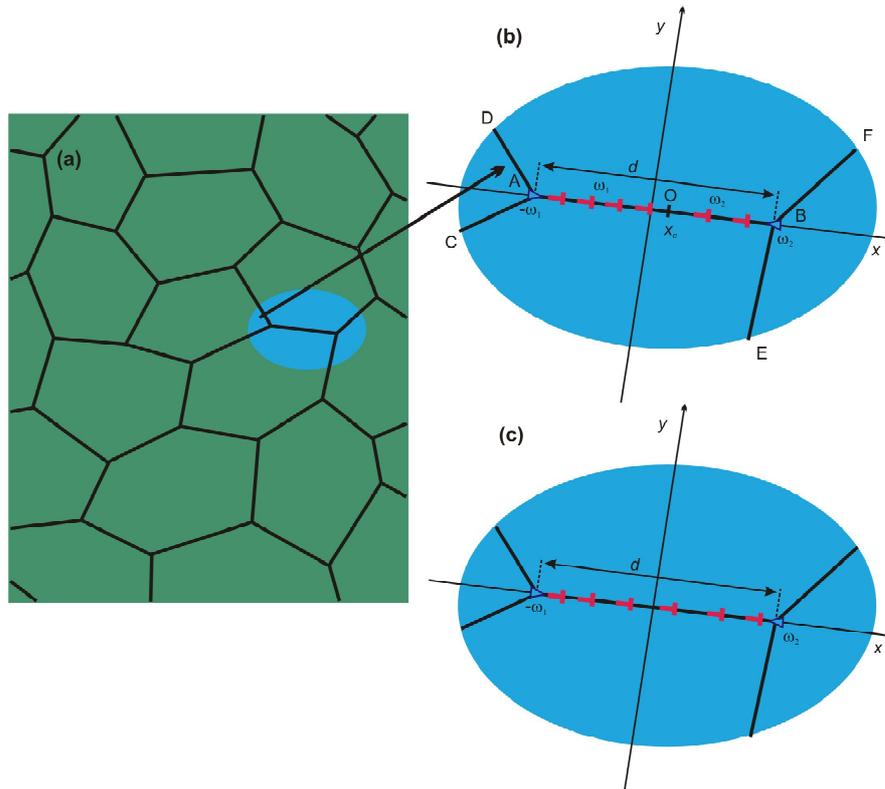


Fig. 1. Grain boundaries in graphene. (a) Polycrystalline graphene sheet consists of grains divided by grain boundaries. General view. (b) Magnified inset shows the grain boundary AB being a wall of perfect dislocations. The grain boundary AB consists of two fragments AO and OB characterized by different dislocation densities and thereby misorientation parameters ω_1 and $-\omega_2$, respectively. The grain boundary ends at triple junctions, A and B, geometrically balanced in the sense that misorientation angles of their adjacent grain boundaries (AC, AD and AO in the case of triple junction A, and BE, BF and BO in the case of triple junction B) are balanced. That is, there are no misorientation angle gaps at the triple junctions, and they do not create internal stresses. In terms of disclination theory, triple junctions A and B contain disclinations with strengths $-\omega_1$ and ω_2 , respectively, that compensate for misorientations of grain boundary fragments AO and OB, respectively (for details, see main text). (c) Magnified inset shows the grain boundary containing perfect dislocations in their equilibrium positions and “compensating” disclinations of strengths $-\omega_1$ and ω_2 at triple junctions.

separating GB fragments with different tilt misorientation angles, whose difference is the disclination strength ω ; see Refs. [15,19,20].

Also, ultrafine-grained metals fabricated by severe plastic deformation methods typically contain large amounts of GBs having rather irregular structures [6-9]. Following the theory of defects, irregular GB structures in ultrafine-grained metals are associated with both high densities of excess GB dislocations irregularly arranged within GBs and corresponding changes of GB misorientation parameters [6-9]. These changes in ultrafine-grained metals are effectively described in terms of partial GB disclinations [21,23]. In doing so, a partial wedge disclinations at a 2D GB in a 3D metal specimen is defined as a line separating 2D GB fragments with different tilt misorientation angles, whose difference is the disclination strength ω ; see Refs. [21-24].

Thus, partial disclinations at GBs often exist in both polycrystalline graphene and ultrafine-grained metals in their as-fabricated states, and GB structures strongly influence the outstanding properties of these advanced materials. In this context, it is very interesting to understand key trends of evolution of disclinated GB structures in specimens of polycrystalline graphene and ultrafine-grained metals after their fabrication. The main aim of this paper is to theoretically describe “equilibrium” structures of initially disclinated GBs in polycrystalline graphene and ultrafine-grained metals, that is, GB structures after their transformations driven by decrease in the elastic energy of GB defects. In doing this, for simplicity and definiteness, we will focus our theoretical examination on structural transformations of

individual GBs with sole partial disclinations (Fig. 1) in their initial states.

2. INHOMOGENEOUS DISLOCATION STRUCTURES OF DISCLINATED GRAIN BOUNDARIES IN POLYCRYSTALLINE GRAPHENE

Let us consider a flat polycrystalline graphene layer consisting of grains divided by grain boundaries (Fig. 1a). In the considered graphene layer, we examine a symmetric tilt grain boundary AB. We focus our analysis on the model situation where the misorientation of the considered low-angle GB is not constant in the entire GB but makes a jump in a point O of the GB line. Following [15,25], we model the low-angle symmetric GB as a wall of perfect dislocations (pentagon-heptagon pairs in graphene hexagonal lattice) whose Burgers vectors are normal to the GB. In this case, the jump of the GB misorientation at point O can be considered as a step-like change of the dislocation density in the GB AB at this point (Fig. 1b).

Let us introduce a Cartesian coordinate system (x,y) in such a way that its origin is located in the middle of the examined GB (Fig. 1b). Let the initial dislocation density in the GB (defined here as the ratio of the dislocation Burgers vector magnitude to dislocation spacing, period of the GB dislocation wall) is equal to ω_1 at $-d/2 < x < x_c$, and to ω_2 at $x_c < x < d/2$, where d is the GB AB length (Fig. 1b).

The grain boundary ends at triple junctions, A and B, located at the points $x = -d/2$ and $x = d/2$ (Figs. 1b and 1c). These junctions in the initial state of the defect configuration under examination are assumed to be geometrically balanced in the sense that misorientation angles of their adjacent grain boundaries (AC, AD, and AO in the case of triple junction A, and BE, BF and BO in the case of triple junction B) are balanced. That is, there are no misorientation angle gaps at the triple junctions, and they do not create internal stresses. In this paper, we focus our theoretical analysis on structural transformations (re-arrangements of GB dislocation structure) of the GB AB, while the neighboring GBs, AC, AD, BE and BF, are treated as those having unchanged dislocation structures. In this case, the role of the neighboring GBs, AC, AD, BE and BF, is in only their contribution to the misorientation balance at the triple junctions A and B. With this role, following the disclination description of triple junctions as stress sources [26,27], the triple junctions A and B can be viewed as those containing wedge disclinations with strengths $-\omega_1$ and ω_2 ,

respectively. In doing so, the disclinations with the strengths $-\omega_1$ and ω_2 compensate for misorientations of grain boundary fragments AO and OB, respectively, in the initial state of the GB AB (Figs. 1b and 1c).

Every dislocation in the GB elastically interacts with the other dislocations and disclinations. We suppose that the force exerted by dislocations and triple junction disclinations on each dislocation leads to dislocation climb over the GB AB and thus the dislocation structure rearrangement. The dislocations climb over the GB until each dislocation reaches its equilibrium position or approaches a triple junction (Fig. 1c). Let us calculate the equilibrium positions of the dislocations in the GB in its final state characterized by the equilibrium dislocation density. To do so, we calculate the projection F_{kx} of the force exerted on the k th dislocation (where $k = 1, \dots, N$, and N is the number of the dislocations in the GB) by other dislocations and triple junction disclinations. The expression for the force projection F_{kx} is obtained using the expressions for the stress fields of dislocations [28] and disclinations [29] in an infinite solid, modified for the case of the plane stress state. This expression has the form

$$F_{kx} = Db_{ky} \left\{ \sum_{\substack{m=1 \\ m \neq k}}^N \frac{b_{my}}{x_k - x_m} - \omega_1 \left(1 + \ln \frac{|x_k + d/2|}{R} \right) + \omega_2 \left(1 + \ln \frac{|x_k - d/2|}{R} \right) \right\}, \quad (1)$$

where $D = E/(4\pi)$, E is the Young modulus, x_k is the position of the k th dislocation, b_{ky} is the projection of the k th dislocation Burgers vector onto the y -axis, and R is the screening length of the disclination stress field. If the coordinates x_k correspond to the equilibrium positions of the dislocations in the GB, then we have: $F_{kx} = 0$, and formula (1) gives

$$\sum_{\substack{m=1 \\ m \neq k}}^N \frac{b_{my}}{x_k - x_m} = \omega_1 \left(1 + \ln \frac{|x_k + d/2|}{R} \right) - \omega_2 \left(1 + \ln \frac{|x_k - d/2|}{R} \right). \quad (2)$$

Let the number of dislocations in the examined GB be large enough ($N \gg 1$). Then we can go from the discrete dislocation wall to a continuous dislocation distribution. We define the dislocation

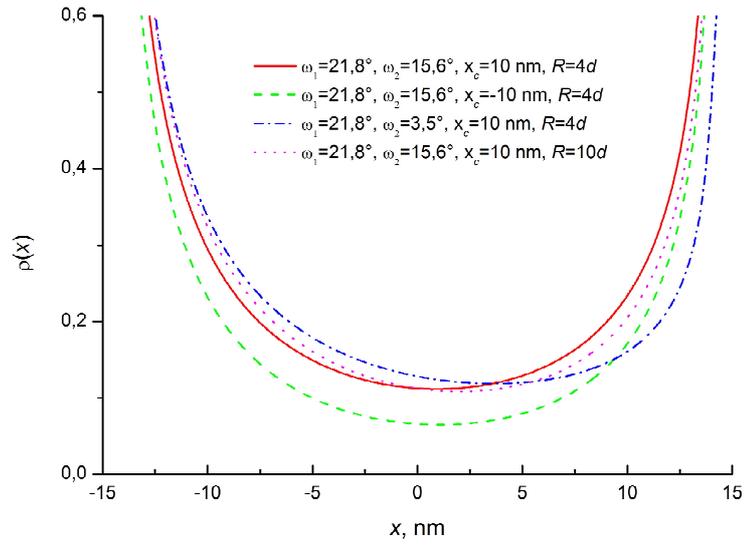


Fig. 2. Dependences of the equilibrium density ρ of the dislocations in the grain boundary in graphene on the coordinate x , for $d = 30$ nm.

density $\rho(x)$ as $\rho(x) = db/dx$. Then formula (2) takes the form

$$\int_{-d/2}^{d/2} \frac{\rho(x') dx'}{x - x'} = \omega_1 \left(1 + \ln \frac{|x_k + d/2|}{R} \right) - \omega_2 \left(1 + \ln \frac{|x_k - d/2|}{R} \right). \quad (3)$$

In the case of $\omega_1 \neq \omega_2$, integral equation (3) has a single solution which is as follows [30]:

$$\rho(x) = -\frac{1}{\pi^2 \sqrt{\frac{d^2}{4} - x^2}} \left[\int_{-d/2}^{d/2} \frac{\sqrt{\frac{d^2}{4} - x'^2} \left\{ \omega_1 \left(1 + \ln \frac{|x' + d/2|}{R} \right) - \omega_2 \left(1 + \ln \frac{|x' - d/2|}{R} \right) \right\}}{x' - x} dx' + C \right], \quad (4)$$

where C is an arbitrary constant. From formulae (3) and (4) it also follows [30] that

$$\int_{-d/2}^{d/2} \rho(x) dx = -\frac{C}{\pi}. \quad (5)$$

From formula (5) and the constancy of the total Burgers vector in the course of dislocation climb over the GB one obtains the following equation that enables one to calculate C :

$$\omega_1 (d/2 + x_c) + \omega_2 (d/2 - x_c) = -\frac{C}{\pi}. \quad (6)$$

Now the equilibrium density $\rho(x)$ of dislocations in the GB is given by formulae (4) and (6). The dependences $\rho(x)$ are presented in Fig. 2 for $d = 30$ nm, $\omega_1 = 21.8^\circ$ and various values of the parameters ω_2 , x_c and R . The values of ω_1 and ω_2 correspond to the misorientation angles of model low-angle GBs formed by regular walls of topological dislocations in graphene [19,25]. As it follows from Fig. 2, the dislocation density $\rho(x)$ increases near the triple junctions with coordinates $x = \pm d/2$. Also, the value of $\rho(x)$ is higher near the disclination of the higher strength, for the same distance from the nearest triple junction. This effect is especially pronounced, when the screening length R of the disclination stress field is high (see Fig. 2).

In the case of $\omega_1 = \omega_2$, Eq. (3), in parallel with the solution given by formula (4), has another simple solution $\rho(x) = \omega_1$. This solution corresponds to a constant density of the GB dislocations and describes the situation where GB dislocations completely eliminate the stress field created by the two triple junction

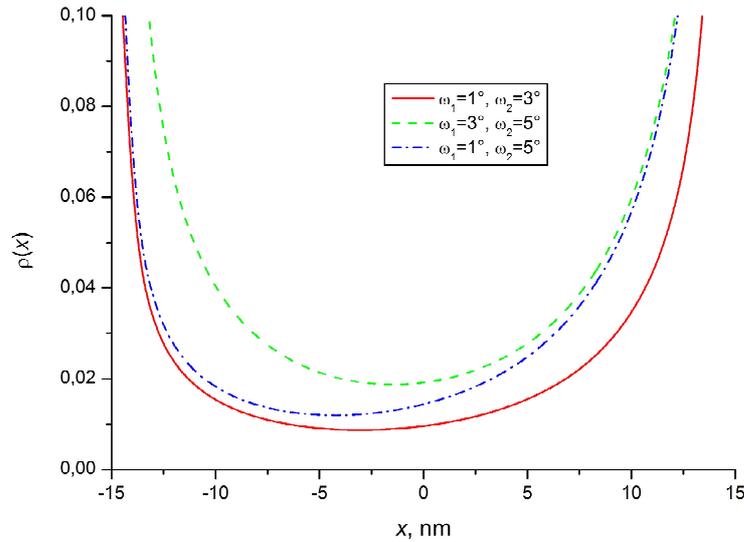


Fig. 3. Dependences of the equilibrium density ρ of the dislocations in the grain boundary in an ultrafine-grained metal on the coordinate x , for $d = 30$ nm, $x_c = 0$ and $R = 4d$.

disclinations. In this case, GB dislocations form a regular dislocation wall, are initially located in their equilibrium positions and thereby do not need to climb.

3. INHOMOGENEOUS DISLOCATION STRUCTURES OF DISCLINATED GRAIN BOUNDARIES IN ULTRAFINE-GRAINED METALS

The previously considered model of GB dislocation climb at the initially disclinated low-angle GBs can also be extended to the case of ultrafine-grained metals. In this case, GB dislocations and disclinations represent linear defects at the 2D GB, and the ultrafine-grained metal is modeled as an infinite solid in the plane strain state. For the discussed case of an infinite three-dimensional solid, all the above formulae remain valid, if one replaces the Young modulus E by $E(1-\nu^2)$, where ν is Poisson's ratio. However, since the equilibrium dislocation density ρ (given by formulae (4) and (6)) does not depend on the elastic moduli E and ν , it does not change in the case of ultrafine-grained metals. Besides, since ρ does not depend on E and ν , the dependences $\rho(x)$ are the same for any ultrafine-grained metal.

The dependences $\rho(x)$ specifying GB dislocation structures in ultrafine-grained metals are presented in Fig. 3, for $d = 30$ nm, $R = 4d$, $x_c = 0$ and various values of the parameters ω_1 and ω_2 . The values of ω_1 and ω_2 correspond to the misorientation angles of low-angle GBs being regular walls of perfect dislocations in an ultrafine-grained metal. As it

follows from Figs. 2 and 3, the character of dislocation distributions in GBs in ultrafine-grained metals is qualitatively similar to that in graphene.

4. CONCLUDING REMARKS

In this paper, a theoretical model was suggested describing structural transformations of GBs initially containing partial wedge disclinations (associated with step-like changes in both GB misorientation and GB dislocation density; see Fig. 1) in polycrystalline graphene and ultrafine-grained metals. Within the model, the transformations occur through GB dislocation climb processes driven by decrease in the elastic energy of GB defect ensemble. It has been theoretically revealed that GB disclinations (being step-like changes in the GB density) in fact spread within GB regions during the structural transformations in question. More precisely, the structural transformations of disclinated GBs in polycrystalline graphene and ultrafine-grained metals result in spatially inhomogeneous distributions of GB dislocations, in which cases GB dislocations tend to form groups with high densities in vicinities of triple junctions (Figs. 2 and 3). (In the absence of pre-existent GB disclinations at a GB, it is specified by a regular periodic distribution of GB dislocations. This is well consistent with numerous experimental data [31].) Such spatially inhomogeneous distributions of GB dislocations at GBs are rather unusual and serve as specific structural features of initially disclinated GBs after their structural relaxation. These specific structural features of GBs are expected to

significantly influence properties of polycrystalline graphene and ultrafine-grained metals.

ACKNOWLEDGEMENTS

This work was supported, in part, by the Russian Ministry of Education and Science (Grants 14.B25.31.0017 and MD-164.2012.1.) and St. Petersburg State University research grant 6.37.671.2013.

REFERENCES

- [1] K.S. Novoselov, A.K. Geim, S.V. Morozov, D. Jiang, Y. Zhang, S.V. Dubonos, I.V. Grigorieva and A. A. Firsov // *Science* **306** (2004) 666.
- [2] A.K. Geim and K.S. Novoselov // *Nature Mater.* **6** (2007) 183.
- [3] A.K. Geim // *Science* **324** (2009) 1530.
- [4] A.H. Castro Nero, F. Guinea, N.M.R. Peres, K.S. Novoselov and A.K. Geim // *Rev. Mod. Phys.* **81** (2009) 109.
- [5] I.A. Ovid'ko // *Rev. Adv. Mater. Sci.* **34** (2013) 1.
- [6] R.Z. Valiev // *Nature Mater.* **3** (2004) 511.
- [7] I.A. Ovid'ko and T.G. Langdon // *Rev. Adv. Mater. Sci.* **30** (2012) 103.
- [8] R.Z. Valiev, I. Sabirov, A.P. Zhilyaev and T.G. Langdon // *JOM* **64** (2012) 1134.
- [9] Y. Estrin and A. Vinogradov // *Acta Mater.* **61** (2013) 782.
- [10] T. Sakai, A. Belyakov, R. Kaibyshev, H. Miura and J.J. Jonas // *Prog. Mater. Sci.* **60** (2014) 130.
- [11] K.V. Emtsev, A. Bostwick, K. Horn, J. Jobst, G.L. Kellogg, L. Ley, J.L. McChesney, T. Ohta, S.A. Reshanov, J. Rohl, E. Rotenberg, A. Schmid, D. Waldmann, H.B. Weber and T. Seyller // *Nature Mater.* **8** (2009) 203.
- [12] A. Reina, X. Jia, J. Ho, D. Hezich, H. Son, V. Bulovic, M.S. Dresselhaus and J. Kong // *Nano Lett.* **9** (2009) 30.
- [13] K.S. Kim, Y. Zhao, H. Jang, S.Y. Lee, J.M. Kim, K.S. Kim, J.-H. Ahn, P. Kim, J.-Y. Choi and B.H. Hong // *Nature* **457** (2009) 706.
- [14] X. Li, W. Cai, J. An, S. Kim, J. Nah, D. Yang, R. Piner, A. Velamakanni, I. Jung, E. Tutuc, S.K. Banerjee, L. Colombo and R.S. Ruoff // *Science* **324** (2009) 1312.
- [15] I.A. Ovid'ko // *Rev. Adv. Mater. Sci.* **30** (2012) 201.
- [16] L.P. Biro and P. Lambin // *New J. Phys.* **15** (2013) 053024.
- [17] P.Y. Huang, C.S. Ruiz-Vargas, A.M. van der Zande, W.S. Whitney, M.P. Levendorf, J.W. Kevek, S. Garg, J.S. Alden, C.J. Hustedt, Y. Zhu, J. Park, P.L. McEuen and D.A. Muller // *Nature* **469** (2011) 389.
- [18] K. Kim, Z. Lee, W. Regan, C. Kisielowski, M.F. Gommie and A. Zettl // *ACS Nano* **5** (2011) 2142.
- [19] I.A. Ovid'ko // *Rev. Adv. Mater. Sci.* **32** (2012) 1.
- [20] I.A. Ovid'ko and A.G. Sheinerman, // *J. Phys. D: Appl. Phys.* **46** (2013) 345305.
- [21] M. Yu. Gutkin and I. A. Ovid'ko, *Plastic Deformation in Nanocrystalline Materials*, (Springer, Berlin, New York, etc., 2004).
- [22] M. Klement and J. Friedel // *Rev. Mod. Phys.* **80** (2008) 61.
- [23] A.E. Romanov and A.L. Kolesnikova // *Prog. Mater. Sci.* **54** (2009) 740.
- [24] S.V. Bobylev, N.F. Morozov and I.A. Ovid'ko // *Phys. Rev. Lett.* **105** (2010) 055504; *Phys. Rev. B* **84** (2011) 094103.
- [25] O.V. Yazyev and S.G. Louie // *Phys. Rev. B* **81** (2010) 195420.
- [26] S.V. Bobylev, M.Yu. Gutkin and I.A. Ovid'ko // *Acta Mater.* **52** (2004) 3793.
- [27] S.V. Bobylev and I.A. Ovid'ko // *Phys. Rev. Lett.* **109** (2012) 175501.
- [28] J.P. Hirth and J. Lothe, *Theory of Dislocations* (Wiley, New York, 1982).
- [29] A.E Romanov and V.I. Vladimirov, In: *Dislocations in Solids*, ed. by F.R.N. Nabarro (North-Holland, Amsterdam, 1992) vol 9, p. 191.
- [30] A.D. Polyaniin and A.V. Manzhirov, *Reference Book on Integral Equations* (Factorial, Moscow, 1998), p. 203 (in Russian).
- [31] A.P. Sutton, R.W. Balluffi, *Interfaces in Crystalline Materials* (Oxford Science Publications, Oxford, 1996).