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To the Question about Migration of Impurity Atoms in Graphene

A.S. Dolgov, Yu.L. Zhabchyk*

Zhukovsky National Airspace University "KhAI", 17, Chkalova Str., 61070 Kharkov, Ukraine

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The uncorrelated accidental jumps of the migration subjects from the allowed positions to the identical immediate ones in the two-dimensional hexagonal structure, which simulates the graphene nodes distribution, are considered. The impurity atoms are placed in the interstitial positions between two atoms of each hexagon side. The offered system corresponds to the sufficiently high temperatures, where the elementary migration act represents the classical over-barrier jump whose probability is defined by the temperature. The exact solution of the unlimited set of the migration microscopic equations is written in the generating function technique and the corresponding microscopic characteristics are found. The anisotropy of the early migration stage can act as an instrument of the matrix state diagnosis and also the formation of the specified impurity geometric structures which are jointed with graphene. The diffusive spread rate, which is compared with the rate of the cellular migration spread, is found. The evolution features of the macroscopic distribution picture of the impurity component on the graphene lattice which are designated by the microscopic geometry impurity atoms displacement are discussed.

Keywords: Graphene, Impurities, Migration, Generating function, Distribution of atoms.

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1. INTRODUCTION

Discovery of graphene [1, 2] was an incitement to theoretical prediction and experimental investigation of the whole set of structure properties and processes in it [3]. A gradual extension of a range of questions which attract attention of the researchers should be considered as one of the tendencies in this field. In particular, the problem of the role of defects of the initial structure is more actualized. It is established experimentally [4] that rather low levels of impurity contamination of graphene lead to the significant change of its characteristics, in particular, one of the most important – conduction that is proposed to use as an indicator of the presence and concentration of impurity atoms [5, 6].

It does not admit of doubt that structure properties depend not only on the total amount of defects but also on their distribution; counter assumption with regard, at least, to some extreme situations would lead to the absurd conclusions. Distribution of impurities fixed in one or another specific situation is the result of the migration processes during the preceding period and can be changed with variation of the conditions: change in the temperature, deformation, introduction of additional sources and sinks. Thus, migration of impurity atoms substantially predetermines a general picture of formed distributions of impurity component and, therefore, important properties of the whole structure as well.

Features of the various migration processes are not covered by simple schemes: variation of the structure and object properties require the use of independent or modified conceptions for different cases. Below we consider one variant of the impurity atom transition in two-dimensional hexagonal structure which simulates the graphene nodes distribution.

2. THE MODEL

The below presented scheme assumes uncorrelated accidental jumps of the migration subjects from the allowed positions to the identical immediate ones. The proposed scheme corresponds to sufficiently high temperatures where the elementary migration act represents classical over-barrier jump, whose probability is defined by the temperature. Whereby, quantum effects which predetermine the possibility of birth of quasiparticles – "impuritons" and corresponding impurity bands are out of the discussion.

Set of tram positions of migrating atoms represents the translation invariant lattice specified by hexagonal structure of graphene. In this case, allowed positions should provide an equality of arrangement with respect to adjacent atoms of the main lattice and, therefore, identity of interaction with these atoms as well. If one is not interested in arrangement of impurity atoms relative to the graphene plane that would make additional sub-variants, then there are only three variants of the arrangement of impurity atoms.

In the structure where impurity atoms are connected with centers of graphene hexagons, a number of nodes of impurity lattice 2 times less than a number of nodes of matrix. This case was studied earlier [7]. If impurity atoms are united with graphene nodes, then set of possible positions of the impurity coincides with graphene lattice [8]. The third variant corresponds to the arrangement of impurity atoms between two atoms of each side of hexagons. In this case, amount of impurity positions is 1.5 times more than graphene nodes. The last circumstance, in particular, is of interest from the point of view of perspectives of the creation of effective accumulators of hydrogen and, possibly, other substances. Hypothetical possibility of total filling of the mentioned positions would provide hydrogen-to-carbon mass ratio equal to 1/8 which is anomalously high value.

* julia.zhabchyk@gmail.com

Based on the aforesaid, the stated type of migration is of an independent interest and is taken as an object for the analysis.

3. GENERAL CORRELATIONS

Each possible position is designated by two indexes; the first index "m" symbolizes change in the numeration along the normal to hexagon sides, and index "n" – along the corresponding sides. In this case, changes in the index by unit correspond to the shift by the value of $(\sqrt{3}/4)a$ along the direction "m" and $(3/4)a$ – along the orthogonal direction.

Transport equations in the dimensionless form are written as follows (for definiteness, reading of the components of position index starts from the position on the side along the "n" direction)

$$\begin{cases} \frac{d\varphi_{4m,4n}}{d\tau} = \varphi_{4m-1,4n-1} + \varphi_{4m-1,4n+1} + \varphi_{4m+1,4n-1} + \\ \quad + \varphi_{4m+1,4n+1} - 4\varphi_{4m,4n}, \\ \frac{d\varphi_{4m-1,4n+1}}{d\tau} = \varphi_{4m-3,4n+1} + \varphi_{4m-2,4n+2} + \varphi_{4m,4n} + \\ \quad + \varphi_{4m+1,4n+1} - 4\varphi_{4m-1,4n+1}, \\ \frac{d\varphi_{4m+1,4n+1}}{d\tau} = \varphi_{4m,4n} + \varphi_{4m-1,4n+1} + \varphi_{4m+2,4n+2} + \\ \quad + \varphi_{4m+3,4n+1} - 4\varphi_{4m+1,4n+1}. \end{cases} \quad (1)$$

Unwritten three equations of (1) are obtained from the first three equations by the corresponding shift of indexes. We should note that choice of the numeration is such that sums of two numbers representing the corresponding position are always even.

Introducing into consideration the Fourier sums (generating functions) G_{00}, G_{11}, $G_{-1,-1}$, G_{22}, $G_{-1,1}$, $G_{1,-1}$ by the general form

$$G_{\alpha\beta}(s_1, s_2, \tau) = \sum_{m,n} \varphi_{4m+\alpha,4m+\beta} e^{i[(4m+\alpha)s_1 + (4m+\beta)s_2]}, \quad (2)$$

where α, β are the integer numbers which specify the reduced set of six values $G_{\alpha\beta}$, we pass from the infinite set of equations (1) to the equivalent system of six equations for $G_{\alpha\beta}$.

Joining functions (2) on grounds of structural unity of the corresponding equations from (1)

$$G_a = G_{00} + G_{22},$$

$$G_b = G_{11} + G_{-1,-1},$$

$$G_c = G_{1,-1} + G_{-1,1},$$

we obtain the system of three equations

$$\begin{cases} \frac{dG_a}{d\tau} = 2\cos(s_1 + s_2)G_b + 2\cos(s_1 - s_2)G_c - 4G_a, \\ \frac{dG_b}{d\tau} = 2\cos(s_1 + s_2)G_a + 2\cos(2s_1)G_c - 4G_b, \\ \frac{dG_c}{d\tau} = 2\cos(s_1 - s_2)G_a + 2\cos(2s_1)G_c - 4G_b. \end{cases} \quad (3)$$

Correlations (3) are the system of the first-order differential equations. Unspecified parameters s_1 and s_2 with the possibility of their arbitrary variation do not influence the qualification of (3) as the equations with constant coefficients.

According to the standard scheme, solutions of (3) are searched in the form of

$$G_a = Ae^{\omega\tau}, \quad G_b = Be^{\omega\tau}, \quad G_c = Ce^{\omega\tau}.$$

Characteristic equation which defines the possible values of ω is the following:

$$g^3 - 4g[\cos^2(2s_1) + \cos^2(s_1 + s_2) + \cos^2(s_1 - s_2)] - \\ - 16\cos(2s_1)\cos(s_1 + s_2)\cos(s_1 - s_2) = 0, \quad (4)$$

where $g \equiv \omega + 4$. Cardano rules allow to write the exact expressions for the roots of (4), however, the last ones are lengthy and hard-to-visible. Moreover, expressions for the roots of (4), valid in the whole actual range of s variation ($0 < |s| < \pi$), are necessary only for the utterly detailed representation of spatial distribution (highly non-uniform artificially formed distributions existing during limited time). As it will be seen subsequently, the predominant interest is connected with the values of s_1, s_2 close to zero.

On the assumption $s_1 = s_2 = 0$, equation (4) has the root $g_1 = 4$ and two coincident roots $g_2 = g_3 = -2$. With taking into account the square additives s_1, s_2, roots of (4) are the following:

$$\omega_1 = -4s_1^2 - \frac{4}{3}s_2^2, \; \omega_{2,3} = -6 + 2s_1^2 + \frac{2}{3}s_2^2. \quad (5)$$

Thus, coincidence of two roots of equation (4) in the region of $|s_1|$, $|s_2| \ll 1$ remains. However, this circumstance does not spread to the whole range of s_1, s_2 variation, wherein it is easy to ascertain taking, for example, that $s_1 = s_2 = \pi/4$. This means that a special form of solutions of the system of equations with constant coefficients arising in such cases should not be considered as a principal feature of the process development and is only the element of the extreme situation.

4. MIGRATION PICTURE

Each function G_a, G_b, and G_c is represented by the sum of three terms, and two of them contain factor $exp(-6\tau)$. Taking into account that unit value of the dimensionless time τ approximately corresponds to the atom stay time in a certain position, we conclude that during the time comparable with the mentioned time interval the stated terms almost decay. This corresponds to a partial elimination of abrupt differences of filling levels of the neighboring positions, weakening of microscopic non-uniformities if they were present in the initial distribution.

Further development of the migration process is covered by the expressions

$$G_a \approx \frac{1}{3}e^{-\left(4s_1^2 + \frac{4}{3}s_2^2\right)\tau},$$

$$G_b \approx \frac{1}{3}\left(1 - \frac{1}{2}s_1^2 + \frac{1}{2}s_2^2 - \frac{1}{3}s_1 s_2\right)e^{-\left(4s_1^2 + \frac{4}{3}s_2^2\right)\tau}, \quad (6)$$

$$G_c \approx \frac{1}{3}\left(1 - \frac{1}{2}s_1^2 + \frac{1}{2}s_2^2 + \frac{1}{3}s_1 s_2\right)e^{-\left(4s_1^2 + \frac{4}{3}s_2^2\right)\tau}.$$

For definiteness, it is accepted that migration subject is in the node (0,0) at the initial moment.

Node possibilities according to the meaning of functions G (2) are defined by the operations of the form

$$\varphi_{mn} = \frac{1}{(2\pi)^2}\iint_{-\pi}^{\pi} G e^{-i(ms_1 + ns_2)} ds_1 ds_2, \quad (7)$$

where that function of G is present which contains node (m,n). For nodes where both numbers representing the position index are even (set "a") correlation (7) has the form of (8), and for other nodes at the same form of the initial introduction of a particle calculations of the type of (9) should be performed. (Terms of expressions (6) proportional to s_1, s_2 do not give the contribution).

$$\varphi_{mn} = \frac{1}{3(2\pi)^2}\iint_{-\pi}^{\pi} e^{-\left(4s_1^2+\frac{4}{3}s_2^2\right)\tau}\cos(ms_1)\cos(ns_2)\,ds_1 ds_2, \quad (8)$$

$$\varphi_{kl} = \frac{1}{3(2\pi)^2}\iint_{-\pi}^{\pi}\left(1-\frac{1}{2}s_1^2+\frac{1}{2}s_2^2\right)\times. \\ \times\ e^{-\left(4s_1^2+\frac{4}{3}s_2^2\right)\tau}\cos(ks_1)\cos(ls_2)\,ds_1 ds_2) \quad (9)$$

Outside the region of ultimately low values of τ, the determinative contribution to the calculations of (8), (9) belongs to small values of s_1, s_2 that is the basis for the above performed simplifications.

Applying integration to infinity, we pass from correlation (8) to expression

$$\varphi_{mn} = \frac{\sqrt{3}}{48\pi\tau}e^{-\frac{m^2+3n^2}{16\tau}}, \quad (10)$$

and formula (9) takes the form

$$\varphi_{kl} = \frac{\sqrt{3}}{48\pi\tau}\left(1-\frac{8\tau-k^2}{128\tau^2}+\frac{24\tau-9l^2}{128\tau^2}\right)e^{-\frac{k^2+3l^2}{16\tau}}. \quad (11)$$

Expressions (10), (11) differ by the factor in brackets, whose difference from unity is significant only for moderate values of τ. This interval can be qualified as a stage of mesoscopic ordering next to the above mentioned stage of microscopic equalizing and, of course, more durational. Within this period one can observe the difference in filling levels of spatially close but owned to different substructures; and formula (10) corresponds to set "a", and sets "b" and "c" in the framework of the performed approximations do not display differences and are described by expression (11).

Values of φ_{kl} asymptotically approach equation (10) but before achievement of asymptotical equality of substructures φ_{kl} can both be less than the value of (10) and exceed it. In this case, sign of the values $(8\tau-k^2)$ and $(8\tau-3l^2)$ is the determinative one. In the region of rather low values of τaccording to (11) contour of the certain level φ_{kl} is an ellipse prolate along the direction "k" (x), and during later periods $(8\tau>k^2)$, $(8\tau>3l^2)$ the stated ellipses are expanded along the direction "l" (y), though, of course, this occurs with total reduction of the filling level that makes the asymmetry effect to be less expressed.

We should emphasize that the change in the sign of expressions $(8\tau-k^2)$ and $(8\tau-3l^2)$ corresponds to the same distance-time relation. The time moment which defines the transition from one variant of ellipticity to another, i.e. corresponding to the density uniformity on the circle of the radius r, is given by the expression:

$$\tau = \frac{3}{2}\frac{r^2}{a^2},$$

where a is the hexagon side.

We note that because of the behavior of the above performed simplifications correlations (10), (11) should not be applied to the conditions when values k, l are too large. Nevertheless, in this region values of functions φ are vanishingly small in comparison with the initial level, and this parameter band is not of interest.

Asymptotic form of the process development corresponds to the period when $\tau > k^2, l^2$. Signs of the substructure inequality disappear on this final stage of the process development. Distribution is locally uniform and follows the laws of macroscopic diffusion.

Root-mean-square deviation of migrating particles from the position of the initial localization is defined as

$$\left(\overline{m^2}\right)^{\frac{1}{2}} = \left(-\frac{\partial^2 G}{\partial s_1^2}(0,0,\tau)\right)^{\frac{1}{2}}$$

and in physical units it is equal to

$$\sqrt{\overline{r^2}} = \sqrt{\frac{3}{2}}a\tau^{\frac{1}{2}} \quad (12)$$

irrespective of the orientation of r direction.

5. CONCLUSIONS

Choice as the investigation object of the migration scheme of a rather specific type was aimed to cover all possible mechanisms of the migration process. Asymptotic form of the diffusion redistribution does not differ qualitatively from that obtained for the cell migration, but quantitative characteristics of comparable processes are different. Ratio of the root-mean-square deviation for the discussed here variant of interstitial positions of migration subjects to the same value corresponding to the cell migration [7] is equal to

$$\frac{\sqrt{3}}{6}\left(\frac{\omega_1}{\omega_0}\right)^{\frac{1}{2}}, \quad (13)$$

where ω_1, ω_0 are the possibilities of jumps in unit time for the mentioned variants of the migration (ω_1 is the characteristic of the given work).

In the cases when difference of the characteristic frequencies ω_1, ω_0 is unessential, the diffuse spreading rate of the initial clot in the considered here situation is substantially less than the same value for cell migration. This is explained, seemingly, by the increased mean density of possible positions and geometry of their arrangement. Thus, analysis of macroparameters of the distribution evolution of diffusion component contains information about both the microscopic migration mechanism and scales of potentials, jump probabilities.

Signs of the distribution anisotropy typical for the relatively early ("pre-asymptotic") evolution stage of the initial distribution can be used both as the diagnostics tool of the matrix state and for the formation of one or another impurity geometric structures jointed with graphene. Naturally, the latter assumes organization of the processes and control on the subatomic or atomic levels that quite corresponds to the problems of modern nanotechnologies.

REFERENCES

1. K.S. Novoselov, D. Jiang, F. Schedin, T.J. Booth, V.V. Khotkevich, S.V. Morozov, A.K.Geim, *PNAS* **102**, 10451 (2005).
2. A.K. Geim, K.S. Novoselov, *Nat. Mater.* **6**, 183 (2007).
3. A.V. Eletskii, *Phys. Usp.* **52**, 209 (2009).
4. Ch. Lee, X. Wei, J.W. Kysar, J. Hone, *Science* **321**, 385 (2008).
5. B. Huang, Z.Y. Li, Z.R. Liu, G. Zhou, S.G. Hao, J. Wu, B.L. Gu, W.H. Duan, *J. Phys. Chem. C* **112**, 13442 (2008).
6. J.H. Chen, C. Jang, E.D. Williams, M.S. Fuhrer, M. Ishigami, *Nat. Phys.* **4**, 377 (2008).
7. A.S. Dolgov, Ju.L. Zhabchyk, *J. Nano- Electron. Phys.* **4** No3, 03021 (2012).
8. A.S. Dolgov, Yu.L. Zhabchyk, *Zh. Nanosystemy, nanomaterialy, nanotekhnologii* **1** No11, (2013).