ПРИКЛАДНАЯ МАТЕМАТИКА И МЕХАНИКА

Вестник Сыктывкарского университета.
Серия 1: Математика. Механика. Информатика.
Выпуск 1 (30). 2019

УДК 548.52

PERCOLATION-NANOCLUSTERS MODEL OF THE CRYSTALLIZATION FRONT

V. N. Cheredov

В работе предложена нанокластерная модель фазового перехода 1-го рода жидкость — твердое тело на основе модели осциллирующих связей и перколяционной решетки связей и узлов. Исследована структура нанокластеров на фронте кристаллизации воды, условия ее возникновения и ее связь с порогом перколяции структуры жидкости. Выявлена связь параметров нанокластеров от соотношения термодинамических и перколяционных характеристик структуры межмолекулярных связей жидкости. В рамках построенной модели изучена динамика структуры решетки воды. Исследованы количественные характеристики нанокластеров жидкой фазы на фронте кристаллизации воды.

Ключевые слова: межмолекулярные связи, фазовые переходы, нанокластеры, порог перколяции, модель осциллирующих связей.

Questions of the study of the structural organization of matter are the focus of attention of physicists, chemists and crystallographers. These issues are of particular relevance due to the intervention of science in the world of nanostructures in recent years and the need to develop new ideas in the description of nanoscale substance.

In this paper, in the development of ideas presented in [1], a new approach is presented in the description of the processes of formation of

a nanocluster structure in liquid water, based on our proposed model of oscillating bonds in the structure of a substance. This approach significantly expands our ability to analyze phase transitions, understanding the nature and structure of the condensed state of matter, the formation of clusters. For the first time, a percolation model of the liquid phase at the water crystallization front has been proposed.

Consider a thermodynamically homogeneous portion of the solid or liquid phase of a substance in a state where all bonds between molecules (atoms) are stable. Since a portion of a substance receives some small amount of heat ΔQ, the internal energy of the molecules U increases by the same value $\Delta U = \Delta Q$. It is quite natural to assume that an increase in the internal energy of molecules can lead to the breaking of certain intermolecular bonds. In general, the breaking of a bond can be represented as a temporary redistribution of the electron density of the atoms forming the molecules and participating in the bond. For example, for a hydrogen and van der Waltz bond, breaking a bond between molecules means a temporary change in the electron density at which one of the molecules participating in the bond loses dipole properties for a time [2].

In this case, a situation may occur when a part of the bonds between molecules in the structure of a substance is in a stable state, and a part of the time in a broken state. And if a substance is in a state with constant temperature and pressure, then a part of the intermolecular bonds is always in a broken state. Broken bonds can be restored, moving to a steady state, and other stable bonds at the same time can break.

Each intermolecular bond in the volume of a substance must oscillate, i.e. break from time to time and then reappear. Moreover, the distribution of broken bonds in space and in time should be uniform A further increase in the internal energy of the molecules increases the number of broken bonds of the H molecule and, accordingly, decreases the number of stable bonds of the F molecule ($F + H = K_m$, where K_m is the coordination number of the molecule). The total internal energy of the molecules and the temperature of a substance depend on the ratio of stable and broken intermolecular bonds.

The remaining bonds of the neighboring molecules slightly displace the molecule in question in space. When the bond is restored, the molecule again occupies its original spatial position. It should be borne in mind that the molecules with which the selected molecule has bonds, themselves also oscillate around the equilibrium position during the oscillation of their bonds. This gives the vibrations of a molecule a chaotic character with degrees of freedom corresponding to the degrees of freedom of thermal vibrations.

The molecules of a substance at $T{=}0\ K$, in order to be released from intermolecular bonds, must be given energy, called the sublimation energy E_s, and equal to:

$$E_s = \frac{i}{2} k_B T_b + \Delta Q_m + \Delta Q_b = K_m \frac{E_m}{2}, \tag{1}$$

where i — the number of degrees of freedom of the sublimated molecule (for three or more atomic molecules is 6), k_B — the Boltzmann constant, T_b - the absolute boiling point, ΔQ_m — the heat of melting per one molecule, ΔQ_b — the heat of vaporization per one, K_m — the coordination number of the molecule in the solid phase, E_m — the bond energy at $= 0\ K$.

Formula 1 shows what energy a substance in the solid phase should have at an absolute zero temperature so that all molecules become free and the molecule from the solid phase passes into the gas, that is, it becomes free from intermolecular bonds. The division by 2 on the right side of Formula 1 arises due to the fact that the breaking of one bond refers immediately to two molecules. In the solid phase, the internal energy of molecules is determined by the energy of their thermal vibrations (the energy of formation and the dynamics of crystal lattice defects [3] are neglected, since it is much less than the latter). The value of the internal energy is found from the experimental data of calorimetric measurements of heat capacity for different phases of a substance and the determination of heat capacity $= dU/dT$, where C — the calorimetric heat capacity. The heat capacity C has a continuous curve within the solid phase of the substance. At the melting temperature $T = T_m$, the heat capacity function has a jump and then within the liquid phase again

has a continuous appearance up to the vaporization temperature [4].

$$F^{sp}\frac{E_m}{2} = K_m\frac{E_m}{2} - U = K_m\frac{E_m}{2} - \int_0^T CdT, \tag{2}$$

where F^{sp} — the number of stable molecular bonds in the solid phase at temperature T. At the melting point $T = T_m$, formula (2) allows calculating the number of stable bonds of the molecule in the solid phase at the melting point F_m^{sp}:

$$F_m^{sp} = K_m - \frac{2}{E_m}\int_0^{T_m} Cdt. \tag{3}$$

In the liquid phase at the melting temperature (crystallization), it is necessary to subtract the heat of melting (given per molecule) from the expression of the binding energy in formula (4).

$$F^{lp}\frac{E_m}{2} = K_m\frac{E_m}{2} - \int_0^T Cdt - \Delta Q_m, \tag{4}$$

where F^{lp} — is the number of stable bonds of the molecule in the liquid phase at T.

Accordingly, we obtain the number of stable bonds of the molecule in the liquid phase F_m^{lp} at the melting point $T{=}T_m$:

$$F_m^{lp} = K_m - \frac{2}{E_m}\int_0^{T_m} Cdt - \frac{2}{E_m}\Delta Q_m. \tag{5}$$

And the number of stable molecular bonds in the liquid phase F_b^{lp} at the boiling point $T{=}T_b$:

$$F_b^{lp} = K_m - \frac{2}{E_m}\int_0^{T_b} Cdt - \frac{2}{E_m}\Delta Q_m. \tag{6}$$

The temperature dependence of the number and proportion of stable molecular bonds for water can be determined by formulas (3) and (4). The numerical data on water required for calculations (melting point and vaporization, specific heat of melting, molecular weight, coordination number, and others) are taken from [5–7]. The temperature dependence of

the heat capacity C_v for ice was taken from [8–10] and water from [11]. For the gaseous phase, the number of stable bonds of the molecule is assumed to be zero. The results are presented in the following figure.

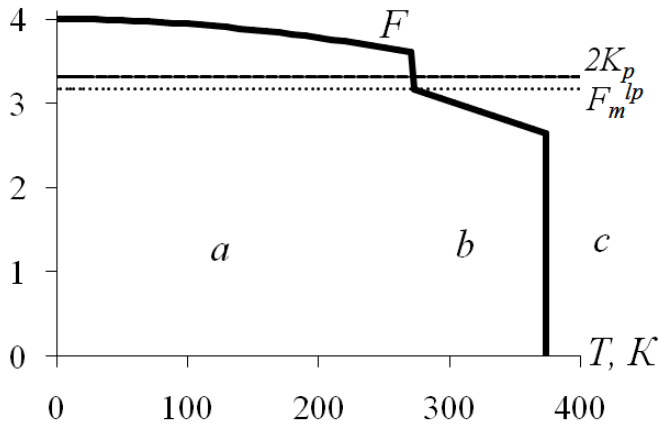

Fig.1. The temperature dependence curve of the stable bonds number molecule F in the $_2$ structure, where K_p — the percolation threshold of the H_2O lattice, a — the solid phase, b — the liquid phase, c — the gaseous phase

Calculations by formulas (3), (5), (6) give for the number of stable bonds of ice at the melting point F_m^{sp}= 3.64. Hence, at the melting point in ice, the molecule has 3.61 stable bonds, and hence 0.36 bonds are broken (with a coordination number of 4). In the liquid phase at the melting point (crystallization) for water we get F_m^{lp} = 3.17, and in the liquid phase at boiling point F_b^{lp} = 2.65.

Clusters of matter in the transition from the vapor phase to the liquid phase, as well as in crystallization processes from supersaturated solutions, have been studied in sufficient detail. In both cases, the cluster molecules are modeled as gas molecules that can spontaneously interlock with each other if the free energy of such a molecular association is less. That is, with and in solutions, cluster molecules are considered as gas molecules in the solvent structure.

Molecules of a monomolecular fluid cannot be dissolved in other molecules of the same fluid, they cannot be free from bonds with other

molecules of a monomolecular fluid. They do not differ from each other. These considerations lead to the conclusion that, at first glance, there can be no molecular associations (clusters) in the volume of a monomolecular fluid. However, the problems of liquid clustering, in particular, at the crystallization front, can be solved within the framework of the percolation theory [12; 13].

The number of stable bonds in molecules of both the solid and liquid phases of a substance at the water crystallization front is obviously half as large as that of molecules of volume. At the melting point in the liquid phase at the crystallization front, the following relationships are true:

$$F_{sur} = \frac{F_m^{lp}}{2} < \frac{F_m^{lp} + \Delta F}{2} = \frac{F_m^{lp}}{2} - \Delta F_p = K_p, \tag{7}$$

where ΔF — the difference in the number of bonds during the percolation and thermodynamic phase transition, $\Delta F_p = K_p - \frac{F_m^{lp}}{2}$ — the decrease in the number of percolation bonds when the bond lattice and nodes are randomized beyond the percolation threshold to the thermodynamic phase transition.

This inequality (7) reflects the condition for the formation of clusters in the liquid phase at the crystallization front of water, in this case clusters are the basis of the structure of the liquid phase at the crystallization front.

In fig. 1 that the number of stable bonds of water molecules in the liquid phase at the melting temperature F_m^{lp} is slightly less than $2K_p$. Clustering in the liquid phase of the water crystallization front is possible, since $F_m^{lp} < 2K_p$. The percolation threshold for water is defined in [14–16].

With a decrease in the number of percolation bonds in the process of randomization of the lattice of bonds and sites beyond the percolation threshold, the cluster sizes decrease and their number increases. Upon reaching a thermodynamic phase transition, a solid-liquid, i.e. when the number of percolation bonds decreases additionally by ΔF_p, nanoclusters have a well-defined size limit [13].

In the model of oscillating bonds, a continuous intermolecular network of bonds of the structure of a liquid does not contradict the existence of

selected nanoclusters in the liquid phase at the crystallization front.

Thus, the occurrence of the crystallization front during the liquid-solid phase transition is a property of the substance self-organization, and the percolation threshold is overcome in a narrow liquid region by forming nanoclusters and incorporating them into the solid phase structure. As noted above, in the bulk, the structure of the liquid is a continuous network of oscillating bonds of molecules and the formation of clusters in it is impossible. Nevertheless, despite the formation in the liquid phase at the crystallization front of nanoclusters, any mentally cut part of the liquid structure is, like the entire volume, a continuous network of oscillating bonds. Fluid, in general, is a stable molecular association. Accordingly, clustering in a liquid does not occur as in gases and supersaturated solutions by combining molecules into associations, but by separating (dissociating) the continuous molecular association into clusters.

Such processes of cluster dissociation are investigated in the theory of percolation [12; 13]. The parameters of such clusters can be determined within the framework of the percolation model of the lattice of links and nodes. The coordination number of the percolation lattice is Km. The order parameter x is determined by the following expression: $x = \frac{F_{sur}}{K_p} = \frac{F^{lp}}{2K_p}$. Order parameter at the percolation threshold: $x_p = 1$.

The universal approximation equation for finding the parameters of clusters in accordance with [12; 13] has the following form:

$$Y_m \infty \mid x_p - x_m \mid^z = \mid 1 - x_m \mid^z = \mid \Delta x_{pm} \mid^z, \tag{8}$$

where Y_m — the cluster parameter (lattice property), x_m — the order parameter of the liquid phase at the crystallization front at the melting temperature ($x_m = \frac{F_m^{lp}}{2K_p}$), z — the topological exponent, Δx_{pm} — the deviation of the order parameter x_m from the order parameter in the percolation threshold x_p, the sign "∞" means direct proportionality with a coefficient in the order of 1. We use, as far as possible, the notation generally accepted in the theory of percolation.

The list of values of exponents z and designations of the parameters of

Table 1

The list of cluster parameters and topological exponentials (exponents of the universal approximation equation) of a 3D lattice with a coordination number $K_m = 4$

Cluster parameters	Cluster parameter designation	Topological exponent designation	Topological exponent value
The average length of the final clusters	$\frac{\overline{L}}{a} = \frac{2r}{a}$	$-\frac{\gamma}{d_f}$	-0.711
Maximum mass (number of nodes) of a finite cluster, d_f — fractal dimension of clusters	$M_{\max}$	$-vd_f$	-2.209
Average mass (number of nodes) of the final cluster	$\overline{M}$	$-\gamma$	-1.795

clusters Y_m for a 3D lattice of links and nodes with a coordination number equal to 4 (corresponds to water) at the point $x = x_m$, in which the order parameter corresponds to the melting temperature, taken from [12; 13] and are summarized in the following table.

Considering that when calculating the F_m^{lp} value according to formula (5), only thermal vibrations are taken into account for expressing the internal energy of molecules (activation and dynamics of crystal structure defects, which contribute substantially less than thermal vibrations to internal energy, are not taken into account), then Δx_{pm} will be a little more and the found parameters of the clusters are the upper bounds for their values

Using the values given in table. 1, according to formula (8), it is easy to plot graphs of dependences of cluster parameters $\frac{L_{max}}{a}$, $\frac{\bar{L}}{a}$, $\bar{M}$ for different values of the order parameter deviation Δx_{pm}.

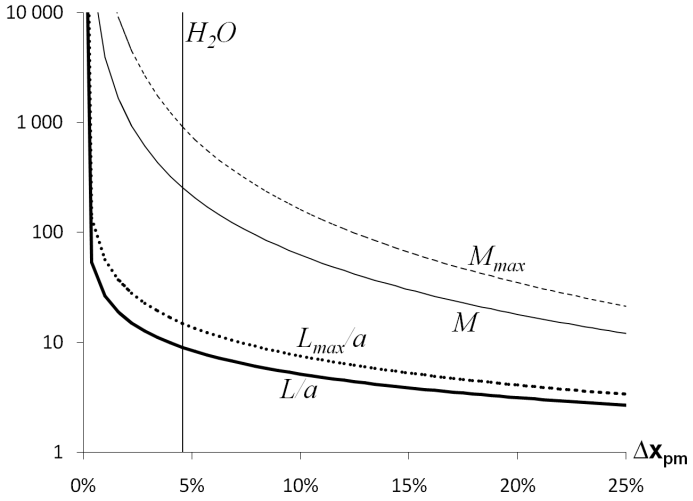

Fig. 2. The dependence curves of the liquid phase clusters parameters on the substance crystallization front at the melting point on the deviation of the order parameter at the percolation threshold Δx_{pm}: the maximum and average mass (number of molecules) in the cluster M_{max}, $\bar{M}$, the maximum and average length (diameter) of the cluster L_{max},$\bar{L}$, expressed in lattice parameters a. The vertical line indicates the parameters of clusters for water

Analysis of the cluster parameters in Fig. 2 shows that as the deviation of the order parameter Δx_{pm} decreases, the length and power of the clusters increase very quickly, and slowly increase with increasing. The singularity in the properties of the lattice begins to manifest itself at values of the deviation of the order parameter Δx_{pm} less than 1% .

For water at the melting temperature (crystallization), the deviation of the order parameter Δx_{pm} is 4.6% . Calculations for water within the framework of the percolation randomized model of knots and bonds give the results noted in Fig. 1. The average and maximum mass of a cluster for water in the liquid phase of the crystallization front is 254 and 911 molecules, respectively. The average and maximum cluster lengths are 9.0 and 14.9 lattice periods, respectively.

Within the framework of the model of oscillating bonds, the structure of the substance in the solid and liquid phase was analyzed as a continuous

oscillating network of bonds homogeneous in the number of stable intermolecular bonds.

The temperature dependence of the number of stable molecular bonds for the solid and liquid phases of a substance, its changes during phase transitions has been revealed.

The formation conditions and parameters of nanoclusters in the liquid phase at the crystallization front were determined.

Список литературы

1. **Чередов В. Н., Куратова Л. А.** Динамика сетки межмолекулярных связей и фазовые переходы в конденсированных средах // *Вестник Сыктывкарского университета. Серия 1: Математика. Механика. Информатика. 2017. 4 (25). С. 20–32.*

2. **Каплан И. Г.** Межмолекулярные взаимодействия. Физическая интерпретация, компьютерные расчёты и модельные потенциалы. М.: БИНОМ. Лаборатория знаний, 2012. 400 с.

3. **Чередов В. Н.** Статика и динамика дефектов в синтетических кристаллах флюорита. СПб: Наука, 1993. 112 с.

4. **Ландау Л. Д., Лифшиц Е. М.** Статистическая физика. М.: Физматлит, 2010. Ч. 1. 616 с.

5. **Енохович А. С.** Справочник по физике и технике. М.: Просвещение, 1989. 224 с.

6. **Зацепина Г. Н.** Физические свойства и структура воды. М.: МГУ, 1998. 184 с.

7. **Эйзенберг Д., Кауцман В.** Структура и свойства воды. М.: Директ-медиа, 2012. 284 с.

8. **Dorsey N. E.** Properties of ordinary Watter-Suvstance. New York: Reinhold Publishing Corporation, 1940. 673 p.

9. **Giauque W. F., Stout J. W.** The entropy of water and the third law of thermodynamics. The heat capacity of ice from 15 to 273°K // *Journal of the American Chemical Society. 1936. V. 58. Pp. 1144–1150.*

10. **McDougall D. P., Giauque W. F.** The production of temperatures below 1° A. The heat capacities of water, gadolinium nitrobenzene sulfonate heptahydrate and gadolinium anthraquinone sulfonate // *Journal of the American Chemical Society. 1936. V. 58. Pp. 1032–1037.*

11. **Кириллин В. А., Сычев В. В., Шендлин А. Е.** Техническая термодинамика. М.: Изд–во МЭИ, 2008. 486 с.

12. **Тарасевич Ю. Ю.** Перколяция: теория, приложения, алгоритмы. М.: Либроком, 2012. 116 с.

13. **Эфрос А. Л.** Физика и геометрия беспорядка. М.: Наука, 1982. 176 с.

14. **Stanley H. E.** A polychromatic correlated-site percolation problem with possible relevance to the unusual behaviour of supercooled H_2O and D_2O [A polychromatic correlated-site percolation problem with possible relevance to the unusual behaviour of supercooled H_2O and D_2O] // *Journal of Physics A: Mathematical and General. 1979. V. 12. 12. Pp. L329–L337.*

15. **Stanley H. E., Teixeira J. J.** Interpretation of the unusual behavior of H_2O and D_2O at low temperatures: Tests of a percolation model [Interpretation of the unusual behavior of H_2O and D_2O at low temperatures: Tests of a percolation model] // *The Journal of Chemical Physics. 1980. V. 73. 7. Pp. 3404–3422.*

16. **Stanley H. E., Teixeira J., Geiger A., Blumberg R. L.** Interpretation of the unusual behavior of H_2O and D_2O at low temperature: Are concepts of percolation relevant to the “puzzle of

liquid wate"? [Interpretation of the unusual behavior of H_2O and D_2O at low temperature: Are concepts of percolation relevant to the"puzzle of liquid water"?] // *Physica A: Statistical Mechanics and its Applications. 1981. V. 106. 1–2. Pp. 260–277.*

Summary

Cheredov V. N. Percolation-nanoclusters model of the crystallization front

A new nanocluster model of a first-order liquid-solid phase transition is proposed based on the model of oscillating bonds and the percolation lattice of bonds and assemblies. The nanocluster structure at the water crystallization front, the conditions of its formation, and its relation to the percolation threshold of the liquid structure are studied. The relationship between the parameters of nanoclusters and the ratio of the thermodynamic and percolation characteristics of the structure of intermolecular fluid bonds has been revealed. Within the framework of the constructed model, the dynamics of the water structure and its phase transitions is studied. Quantitative characteristics of liquid phase nanoclusters at the water crystallization front are studied.

Keywords: intermolecular bonds, phase transitions, nanoclusters, percolation threshold, model of oscillating bonds.

References

1. **Cheredov V. N., Kuratova L. A.** Dinamika setki mezhmolekulyarnyh svjazej i fazovyje perehody v kondensirovannyh sredah (Dynamics of a network of intermolecular bonds and phase transitions in condensed matter), *Bulletin of Syktyvkar University*, Series 1: Mathematics. Mechanics. Informatics, 2017, 4(25), pp. 20–32.

2. **Kaplan I. G.** *Mezhmolekuljarnye vzaimodejstvija. Fizicheskaja interpretacija, komp'juternye raschjoty i model'nye potencialy* (Intermolecular interactions. Physical interpretation, computer calculations and model potentials), M.: BINOM, Laboratorija znanij, 2012, 400 p.

3. **Cheredov V. N.** *Statika i dinamika defektov v sinteticheskih kristallah fljuorita* (Statics and dynamics of defects in synthetic fluorite crystals), SPb: Nauka, 1993, 112 p.

4. **Landau L. D., Lifshic E. M.** *Statisticheskaja fizika. Ch.1* (Statistical physics. Part 1), M.: Fizmatlit, 2010, 616 p.

5. **Enohovich A. S.** *Spravochnik po fizike i tehnike* (Reference book on physics and techniques), M.: Prosveshhenie, 1989, 224 p.

6. **Zacepina G. N.** *Fizicheskie svojstva i struktura vody* (Physical properties and structure of water), M.: MGU, 1998, 184 p.

7. **Jejzenberg D., Kaucman V.** *Struktura i svojstva vody* (Structure and properties of water), M.: Direkt-media, 2012, 284 p.

8. **Dorsey N. E.** *Properties of ordinary Watter-Suvstance*, New York: Reinhold Publishing Corporation, 1940, 673 p.

9. **Giauque W. F., Stout J. W.** The entropy of water and the third law of thermodynamics. The heat capacity of ice from 15 to 273°K, *Journal of the American Chemical Society*, 1936, V. 58, pp. 1144–1150.

10. **McDougall D. P., Giauque W. F.** The production of temperatures below 1° A. The heat capacities of water, gadolinium nitrobenzene sulfonate heptahydrate and gadolinium anthraquinone sulfonate, *Journal of the American Chemical Society*, 1936, V. 58, pp. 1032–1037.

11. **Kirrilin V. A., Sychev V. V., Shendlin A. E.** *Tekhnicheskaya termodinamika* (Technical thermodynamics), Moscow: Izdatelstvo MEI, 2008, 486 p.

12. **Tarasevich Ju. Ju.** *Perkoljacija: teorija, prilozhenija, algoritmy* (Percolation: theory, applications, algorithms), M.: Librokom, 2012. 116 p.

13. **Jefros A. L.** *Fizika i geometrija besporjadka* (Physics and geometry of disorder), M.: Nauka, 1982, 176 p.

14. **Stanley H. E.** A polychromatic correlated-site percolation problem with possible relevance to the unusual behaviour of supercooled H_2O and D_2O (A polychromatic correlated-site percolation problem with possible relevance to the unusual behaviour of supercooled H_2O and D_2O), *Journal of Physics A: Mathematical and General*, 1979, V. 12, 12, pp. L329–L337.

15. **Stanley H. E., Teixeira J. J.** Interpretation of the unusual behavior of H_2O and D_2O at low temperatures: Tests of a percolation model (Interpretation of the unusual behavior of H_2O and D_2O at low temperatures: Tests of a percolation model), *The Journal of Chemical Physics*, 1980, V. 73, 7, pp. 3404–3422.

16. **Stanley H. E., Teixeira J., Geiger A., Blumberg R. L.** Interpretation of the unusual behavior of H_2O and D_2O at low temperature: Are concepts of percolation relevant to the "puzzle of liquid wate"? (Interpretation of the unusual behavior of H_2O and D_2O at low temperature: Are concepts of percolation relevant to the"puzzle of liquid water"?), *Physica A: Statistical Mechanics and its Applications*, 1981, V. 106, 1–2, pp. 260–277.

Для цитирования: Чередов В. Н. Перколяционно-нанокластерная модель фронта кристаллизации // *Вестник Сыктывкарского университета. Сер. 1: Математика. Механика. Информатика. 2019. Вып. 1 (30). С. 53–66.*

For citation: Cheredov V. N. Percolation-nanoclusters model of the crystallization front, *Bulletin of Syktyvkar University. Series 1: Mathematics. Mechanics. Informatics*, 2019, 1 (30), pp. 53–66.

СГУ им. Питирима Сорокина *Поступила 11.03.2019*