УДК 544.344.4
doi: 10.18101/ 978-5-9793-0898-2-36-44

FROM STATE PHASE DIAGRAMS GRAPHICS COMPILATION TO THE COMPUTER SPACE MODELS ASSEMBLING

© ***V. I. Lutsyk***, Doctor of Chemical Science, Professor,
Buryat State University,
Institute of Physical Materials Science SB RAS
24a Smolina St., Ulan-Ude, Russia
E-mail: vluts@ipms.bscnet.ru

Ideas to assemble the constitutional phase diagrams (PD) as a set of its surfaces or phase regions are discussed. Computer space models of PD became the effective tool of materials science.
Keywords: phase diagram assembling, space model, complex, simplex, polyhedration, 3(4)-phase regions with the reaction type changing, calculation of mass balances.

First Dean of the Chemical Department of the Donetsk State University professor Marx V. Mokhosoev has written, that he had left a part of his heart in Donetsk (Ukraine) [1]. Fifty years ago, in 1966, he had given for his first-year students (freshmen) the project's titles on the inorganic chemistry to compile the data on the constitutional phase diagrams (PD). As a result, 12 years later the handbook on the molybdate and tungstate systems has been published [2].

First experiments in the field of multi-component systems by a young research team in Donetsk were devoted to the systems of sulphates, molybdates, vanadates, phosphates and molybdenum anhydride (under the leadership of I.F. Kokot, B.V. Slobodin and G.G. Koshcheev). Later many students were engaged in this work in the lab room number 108 of the new chemical department building. Valery Artyemov burned on wood a portrait of the Academician Nickolay Kurnakov as a logo of our young research team in the lab room #108. That time we didn't yet know about the mystery and auspicious of this number [3].

Students Valery Mank and Valentina Makarevskaya spent many evenings in the room #108 and were most successive publishing their results [4-5]. The dreams of this student team were realized later in Ulan-Ude by the computer-aided materials design sector of the Institute of

Physical Materials Science (Siberian Branch of the Russian Academy of Sciences) [6]: http://ipms.bscnet.ru/labs/skkm.html

First achievements were summarized earlier [7,8] at the Institute of the Natural Sciences (Siberian Branch of the USSR Academy of Sciences) under the auspices of the USSR Academy of Sciences corresponding-member Marx V. Mokhosoev and professor Kuz'ma A. Nikiforov, and new tasks were formulated [9,10]. Both monographs [7,8] contain the software listings as the supplement.

Geometric and thermodynamic myths of the PD researchers may be rescinded by means of the space computer models [11]. Space models of multi-dimensional PD of multi-component systems are popularized as a novel tool of materials scientists and metallurgists [12-13].

Different types 3D and 4D PD of the hypothetical and real ternary and quaternary systems were assembled from their (hyper)surfaces or phase regions [14-30].

Participants of the 22^{d} All-Russian student scientific conference were acquainted with the materials heredity decoding by the PD computer space models [31]. Young generation of the Russian engineers and their colleagues from abroad studied the phase diagram as a tool of materials science [32].

Student business [33,34] is invited to manufacture the so called exploded phase diagrams as the 3D puzzle of their phase regions. In the same manner the subsystems would be the puzzles of the quaternary reciprocal systems in the process of their tetrahedration.

New ideas wait their implementation. Main task is to change a kinematical surface [9] by a surface with the minimal area. In this case information about binary systems is used to the maximum extent and does not require an experiment inside the surface contour (Fig. 1a). It boils down to the task of defining the surface $Z = Z(x, y)$ with the specified bounds.

Consider smooth surface properties, e.g. liquidus temperature of continuous series of solid solutions in the system A-B-C. Since the nature of the surface we don't know, let's say that its average curvature $H = 0$, i.e. it is a surface which among other surfaces with the same borders has a minimal area. We came to the task of finding the minimum surface to a specified boundary, called the Plateau's problem [35,36]. Plateau's problem is to show the existence of a minimal surface with a given boundary, a problem raised by J.-L. Lagrange in 1760. However, it is named after

Joseph Plateau, who experimented with soap films. The problem is considered part of the calculus of variations.

Various specialized forms of the problem were solved, but it was only in 1930 that general solutions were found in the context of mappings (immersions) independently by Jesse Douglas and Tibor Radó. Their methods were quite different; Radó's work built on the previous work of René Garnier and held only for rectifiable simple closed curves, whereas Douglas used completely new ideas with his result holding for an arbitrary simple closed curve. Both relied on setting up minimization problems; Douglas minimized the now-named Douglas integral while Radó minimized the "energy".

So, the average curvature of a surface is defined as [7, pages 98-100]:

$$H=\frac{1}{2}\,\frac{EN-2FM+GL}{EG-F^2},$$

where $E=1+z_x^2$; $G=1+z^2_y$; $F=z_xz_y$; $L=Z_{xx}/\sqrt{1+z_x^2+z_y^2}$;

$M=Z_{xy}/\sqrt{1+z_x^2+z_y^2}$; $N=Z_{yy}/\sqrt{1+z_x^2+z_y^2}$.

Following the hypothesis that n = 0, we get

$$\frac{ÅN-2FM+GL}{EG-F^2}=0 \text{ or } \frac{\left(1+z_x^2\right)z_{yy}-2z_xz_yz_{xy}+\left(1+z_y^2\right)z_{xx}}{\left(1+z_x^2+z_y^2\right)^{3/2}}=0.$$

Because the denominator is positive and is not equal to zero, we have the equation

$$(1+z_x^2)z_{yy}-2z_xz_yz_{xy}+(1+z_y^2)z_{xx}=0, \qquad (1)$$

the solution of which is our task.

This is a nonlinear differential equation of second degree with partial derivatives of elliptic type. If a self-contained formula for the solution is not available, the solution may be numerically approximated using computers. The theory of dynamical systems puts emphasis on qualitative analysis of systems described by differential equations, while many numerical methods have been developed to determine solutions with a given degree of accuracy.

Put a ternary system with smooth surface of property in rectangular Cartesian coordinate system as shown in Fig. 1. Let forming it binary systems represent curves described by equations respectively $z_{A-B}=\varphi_1(x,y)$, $z_{B-C}=\varphi_2(x,y)$ and $z_{A-C}=\varphi_3(x,y)$. At the specified contour the surface $z=z(x,y)$ are to be find, which is the solution of equation (1). Numerical methods are used. To do this, apply to the triangle A-B-C the

uniform grid with step λ formed by lines parallel to the sides of the triangle. Consider an arbitrary node on the grid with number ijk (Fig. 1b). For the taken composition the content of the component B changes on axis *i*, the component A — on axis *j* and the component C — on the axis *k*. For newly imposed axes a, b, c will get

$$\frac{\partial z}{\partial x}=\frac{\partial z}{\partial a};\qquad \frac{\partial^2 z}{\partial x^2}=\frac{\partial^2 z}{\partial a^2};\qquad \frac{\partial z}{\partial y}=\frac{1}{\sqrt{3}}\left(\frac{\partial z}{\partial b}+\frac{\partial z}{\partial c}\right);$$

$$\frac{\partial^2 z}{\partial y^2}=\frac{2}{3}\left(\frac{\partial^2 z}{\partial b^2}+\frac{\partial^2 z}{\partial c^2}-\frac{1}{2}\frac{\partial^2 z}{\partial a^2}\right)\frac{\partial^2 z}{\partial x\partial y}=\frac{1}{\sqrt{3}}\left(\frac{\partial^2 z}{\partial b^2}-\frac{\partial^2 z}{\partial c^2}\right)$$

and equation (1) rewrite as

$$\frac{2}{3}\left[1+\left(\frac{\partial z}{\partial a}\right)^2\right]\left(\frac{\partial^2 z}{\partial b^2}+\frac{\partial^2 z}{\partial c^2}-\frac{1}{2}\frac{\partial^2 z}{\partial a^2}\right)+\left[1+\frac{1}{3}\left(\frac{\partial z}{\partial b}+\frac{\partial z}{\partial c}\right)^2\right]\frac{\partial^2 z}{\partial a^2}-\frac{2}{3}\frac{\partial z}{\partial a}$$

$$\left(\frac{\partial z}{\partial b}+\frac{\partial z}{\partial c}\right)\left(\frac{\partial^2 z}{\partial b^2}-\frac{\partial^2 z}{\partial c^2}\right)=0.$$

Replace partial derivatives through central-difference scheme for a node ijk:

$\partial z/\partial a=(z_{i,j+1,k-1}-z_{i,j-1,k+1})/2\lambda;$

$\partial z/\partial b=(z_{i+1,j+1,k}-z_{i-1,j-1,k})/2\lambda;$

$\partial z/\partial c=(z_{i+1,j,k+1}-z_{i-1,j,k-1})/2\lambda;$

$\partial^2 z/\partial a^2=(z_{i,j+1,k-1}+z_{i,j-1,k+1}-2z_{ijk})/\lambda^2$

$\partial^2 z/\partial b^2=(z_{i+1,j+1,k}+z_{i-1,j-1,k}-2z_{ijk})/\lambda^2$

$\partial^2 z/\partial c^2=(z_{i+1,j,k+1}+z_{i-1,j,k-1}-2z_{ijk})/\lambda^2$

Get a system of the K equations of the type

$$\frac{2}{3}\left[1+\frac{\left(z_{i,j+1,k-1}-z_{i,j-1,k+1}\right)^2}{4\lambda^2}\right]\times$$

$$\times$$

$$\left(\frac{z_{i+1,j+1,k}+z_{i-1,i-1,k}-2z_{ijk}}{\lambda^2}+\frac{z_{i+1,j,k+1}+z_{i-1,j,k-1}-2z_{ijk}}{\lambda^2}-\frac{z_{i,j+1,k-1}+z_{i,j-1,k+1}-2z_{ijk}}{2\lambda^2}\right)+$$

$$+\left[1+\frac{\left(z_{i+1,j+1,k}-z_{i-1,j-1,k}+z_{i+1,j,k+1}-z_{i-1,j,k-1}\right)^2}{12\lambda^2}\right]$$

$$\frac{z_{i,j+1,k-1}+z_{i,j-1,k+1}-2z_{ijk}}{\lambda^2}-\frac{2}{3}\frac{\left(z_{i,j+1,k-1}-z_{i,j-1,k+1}\right)}{4\lambda^2}\times$$

$$\times\frac{\left(z_{i+1,j+1,k}-z_{i-1,j-1,k}+z_{i+1,j,k+1}-z_{i-1,j,k-1}\right)}{4\lambda^2}\times$$

$$\frac{z_{i+1,j+1,k}-z_{i-1,j-1,k}-z_{i+1,j,k+1}-z_{i-1,j,k-1}}{\lambda^2}=0,$$

where for the sides of the triangle splitting into N equal segments, number of unknown nodes inside the triangle is computed as

$$K=\sum_{i=1}^{N-2}(N-i-1).$$

System's solution — temperature values to the given node inside a triangle — will be get by the Newton's method. As the initial approximations are accepted the values of temperatures in the nodes of the grid, obtained for the plane, which was built on three points: A(0, 0, T_A), B(1/2, $\sqrt{3/2}$, T_B), C(1, 0, T_c) (Fig.1a). An algorithm is realized in the program MIN, where each node within the triangle ijk is surrounded by six others: (i–1)-th, (i+1)-th, (j–1)-th and (j+1)-th, (k–1)-th and (k+1)-th (Fig. 1b). Consequently in all these nodes seven derivatives are calculated and the value of the function in the node ijk, when a system of K linear equations is solved using the standard procedure.

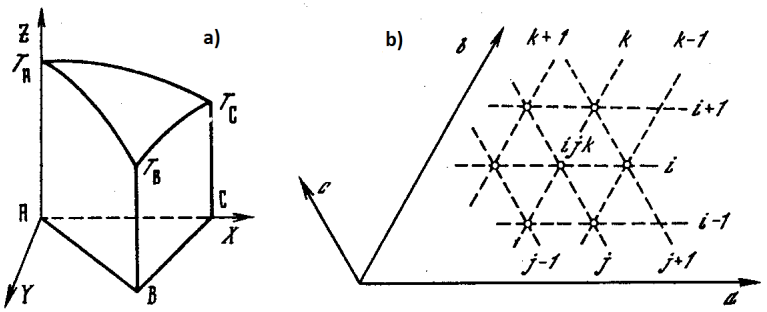

Fig. 1. System A-B-C with smooth surface — (a) and central-difference scheme to solve equation (1) — (b)

Supported by the program of fundamental research SB RAS (project 0336-2014-0003) and partially supported by the Russian Foundation for Basic Research (projects 14-08-00453, 15-43-04304).

References

1. We remember him so… / Devoted to the 70th Anniversary of the Corresponding-member of the USSR Academy of Sciences M.V. Mokhosoev. Ulan-Ude: BSC Publ. House. 2002. P. 39. (In Russian)

2. MokhosoevM.V., Alekseev F.P., Lutsyk V.I. Constitutional phase diagrams of the molybdate and tungstate systems. Novosibirsk: Nauka Publ. House, Siberian Branch, 1978. 319 p. (In Russian)

3. Gilbert E. Eat, Pray, Love: One Woman's Search for Everything across Italy, India and Indonesia. Bloomsburypbks (#1 New York Times bestseller). 2006. P. 7.

4. Lutsyk V.I., Mank V.V., MokhosoevM.V. Surface of primary crystallization in ternary system Li_2SO_4-K_2SO_4-MoO_3 // J. Inorgan. Chem. 1977. V. 22, № 10. P. 2827-2830. (In Russian)

5. Lutsyk V.I., Makarevskaya V.V. Fusing diagrams of system K_2SO_4-Cs_2SO_4-MoO_3 // USSR Academy of Sci. Proceedings. Inorganic Materials. 1978. V. 14, № 3. P. 932-934. (In Russian)

6. Site of the computer-aided materials engineering sector IPMS SB RAS http://ctj.isuct.ru/?q=node/2047 http://ipms.bscnet.ru/labs/skkm.html http://ctj.isuct.ru/files/2012/v55 n09 2012 abstracts en.pdf .

7. Lutsyk V.I. Liquidus surface analysis in the ternary systems. Moscow: Nauka Publ. House. 1987. 150 p. (In Russian)

8. Lutsyk V.I., Vorob'eva V.P., Sumkina O.G. Simulation of the quaternary systems phase diagrams. Novosibirsk: Nauka Publ. House (Siberian Branch). 1992. 199 p. (In Russian)

9. Lutsyk V.I., Zelenaya A.E., Zyryanov A.M. Multicomponent systems simulation by the software of "Diagrams Designer" // J. Materials, Methods & Technologies. Intern. Scientific Publ. 2008. V. 2. Part 1. P. 176-184.

10. Lutsyk V.I., Vorob'eva V.P. Relation between the Mass-Centric Coordinates in the Multicomponent Salt Systems //Z. Naturforsch. A. 2008. V. 63a. No 7-8. P. 513-518.

11. Lutsyk V.I. Geometric and thermodynamic myths of the phase diagrams researchers // Abstr. III International conference HighMatTech. Kiev. 2011. P. 70.

12. Lutsyk V. Space models of constitutional diagrams as a new tool of materials science // Proceed. XV Khariton's topical scientific readings. International Conference "Extreme states of substance. Detonation. Shock waves". Sarov, 2013. P. 230-233.

13. Lutsyk V. Phase diagram as a tool of metallurgist and materials scientist // Proceed. 46th Intern. October Conf. on Mining and Metallurgy. Bor, Serbia. 2014. P. 148-151.

14. Lutsyk V.I., Vorob'eva V.P. Computer models of eutectic type T-x-y diagrams with allotropy. Two inner liquidus fields of two low-temperature modifications of the same component // J. Thermal Analysis and Calorimetry. 2010. V. 101. No 1. P. 25-31.

15. Lutsyk V., Zelenaya A. Computer model for T-x-y diagram with a binary compound decomposed at high temperatures // ECS Transactions. 2010. V. 25. No 25. P. 31-41.

16. Lutsyk V.I., Vorob'eva V.P. T-x-y Diagrams Computer Models for Lead-Free Soldering Systems // *IOP Conf. Ser.: Mater. Sci. Eng. 2011. V.* 18. No 9.http://iopscience.iop.org/1757-899X/18/9/092016/pdf/1757-899X_18_9_092016.pdf.

17. Lutsyk V.I., Vorob'eva V.P. Matrix solution for Polyhedration of Na-K-Ca-Cl-N-O, Na-K-Mo-W-F-O and Na-Ba-B-F-O Systems // *IOP Conf. Ser.: Mater. Sci. Eng. 2011. V.* 18. No 22. http://iopscience.iop.org/1757-899X/18/22/222005/pdf/1757-899X_18_22_222005.pdf.

18. Lutsyk V.I., Sumkina O.G., Savinov V.V., Zelenaya A.E. Precision of the eutectic points determination by the isopleths // *IOP Conf. Ser.: Mater. Sci. Eng. 2011. V.* 18. No 16. http://iopscience.iop.org/1757-899X/18/16/162021/pdf/1757-899X_18_16_162021.pdf

19. Lutsyk V., Zelenaya A. Improvement of the Method to Search Low-melting Solvents for the Crystals $MBaNa(BO_3)_2$ (M=Sc,Y) Growth // Solid State Sciences. 2012. V. 14, Issues 11-12, P. 1604-1608.

20. Lutsyk V.I., Zelenaya A.E., Zyryanov A.M. Search of Low-Temperature Solvents Using Nonplanar Tie-Lines // Crystallography Reports. 2012. V. 57. No 7. P. 111-114.

21. Lutsyk V.I., Vorob'eva V.P., Sumkina O.G. Triangulation of Salt Systems with Barium Borate // Ibid. P. 115–125.

22. Lutsyk V., Vorobjeva V., Parfenova M. Quaternary Reciprocal Systems with the Inner Diagonals: Variants of Polyhedration // Advanced Materials Research. 2013. V. 704. P. 55-60.

23. Lutsyk V.I., Vorobeva V.P., Sumkina O.G., Lamueva M.V. Polyhedration of Multicomponent Mineral Systems // IFAC Proceedings Volumes (IFAC-PapersOnline). 2013. V. 15 (Part 1). P. 288-293.

24. Lutsyk V.I., Vorobeva V.P., Zyryanov A.M., Shodorova S.Y. Correction of T-x-y Diagrams for Lead-Free Solders // Ibid. P. 371-376.

25. Lutsyk V.I., Vorob'eva V.P. (2014) Algorithm for Topological Correction of Lists of Simplexes of Different Dimensions for Polyhedration of Multicomponent Systems // Russ. J. Inorg. Chem. 2014. V. 59. P. 956–970.

26. Lutsyk V.I., Vorob'eva V.P. Search for Internal Diagonals in Polyhedration of Reciprocal Systems by the Algorithm for Topological Correction of Lists

of Simplexes of Different Dimensions // Russ. J. Inorg. Chem. 2014. V. 59, No. 10. P. 1123–1137.

27. Lutsyk V.I., Vorob'eva V.P. Three-Dimensional Model of Phase Diagram of Au–Bi–Sb System for Clarification of Thermodynamic Calculations // Russ. J. Phys. Chem. A. 2015. V. 89. P. 1715-1722.

28. Lutsyk V.I., ZelenayaA.E. 4D space models of quaternary systems for the phase diagrams graphics correction // IOP Conf. Series: Materials Science and Engineering. 2016. V. 123. 012036 doi:10.1088/1757-899X/123/1/012036. P. 1-4.

29. Lutsyk V.I., Vorob'eva V.P. Topological Correction of Multicomponent Systems Polyhedration // Ibid. 012037 doi:10.1088/1757-899X/123/1/012037. P. 1-4.

30. Lutsyk V.I., Vorob'eva V.P., Shodorova S.Ya. Verification of the T-x-y Diagram of the Ag-Au-Bi System Using a 3D Computer Model // Russ. J. Inorg. Chem. 2016. V. 61. P. 858-866.

31. http://asf.ural.ru/VNKSF/Orgcomitet/science_v22.html (Materials Science — 18) http://asf.ural.ru/VNKSF/Program/plenum.html (Materials Science — 18) http://asf.ural.ru/VNKSF/Itogi/re_v22/Nauka/Analisist-otchet-VNKSF-22.pdf

http://asf.ural.ru/VNKSF/Tezis/v22/Programmka-VNKSF-22.pdf (Materials Science — 18)

32. Lutsyk V.I. Computer models of T-x-уиT-x-y-z diagrams to decide the applied and fundamental problems of materials science: Educational service of the International youth industrial engineers Forums «Engineers of Future» http://www.enfuture.ru/enfuture/c15 http://www.enfuture.ru/enfuture/c21 http://www.enfuture.ru/services/23 .

33. http://www.miramodus.com

34. Lutsyk V.I., Vorobjeva V.P., Parfenova M.D. Students' business in chemical education and materials science // II Intern. Scientific-practical conference "Innovative Perspectives of Donbass". V. 4. Donetsk: DSTU Publ. House, 2016. P. 115-119.

35. https://en.wikipedia.org/wiki/Plateau%27s_problem

36. Harrison J. Soap Film Solutions to Plateau's Problem // J. Geom. Analysis. 2012. V. 24. P. 271-297.

ОТ КОМПИЛЯЦИИ ГРАФИКИ К СБОРКЕ КОМПЬЮТЕРНЫХ ПРОСТРАНСТВЕННЫХ МОДЕЛЕЙ ФАЗОВЫХ ДИАГРАММ СОСТОЯНИЯ

В. И. Луцык, доктор химических наук, профессор,
заведующий сектором компьютерного конструирования материалов
Институт Физического материаловедения СО РАН,
профессор кафедры общей и аналитической химии БГУ,

Россия, 670000, Улан-Удэ, ул. Смолина, 24а
E-mail: vluts@ipms.bscnet.ru

Обсуждаются проблемы сборки многомерных пространственных фазовых диаграмм (ФД) состояния многокомпонентных систем. Компьютерные пространственные модели ФД становятся эффективным инновационным инструментом материаловедения.
Ключевые слова: сборка фазовых диаграмм, пространственные модели, комплекс, симплекс, поолэдрация, 3(4)-фазные области со сменой типа реакции, расчет материальных балансов