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A FAMILY OF RECURRENCE GENERATED PARAMETRIC FUNCTIONS BASED ON VOLMER-WEBER-KAISHEW ACTIVATION FUNCTION*

Nikolay Kyurkchiev

The Volmer theory is correct in predicting a dependence of critical supersaturation on contact angle in heterogeneous nucleation. In this paper we consider dependence of supersaturation on contact angle by a family of recurrence generated parametric functions based on the Volmer–Weber–Kaishew activation function (VWKAF).

1. Introduction

The understanding of nucleation theory has been dominated for almost 90 years by classical nucleation theory (see, Volmer and Weber [1], Volmer [2], Becker and Doring [3], Frenkel [4], Zeldovich [5]).

Condensation and evaporation, crystal growth are only a few of the processes in which nucleation plays a prominent role (see, Kashchiev [12], Dubrovskii [13], Bentea, Watzky and Finke [15]). The classical (simple) scheme is:

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Key words: Volmer–Weber–Kaishew activation function (VWKAF), contact angle, recurrence generated family, shifted Heviside function, Hausdorff distance, upper and lower bounds.

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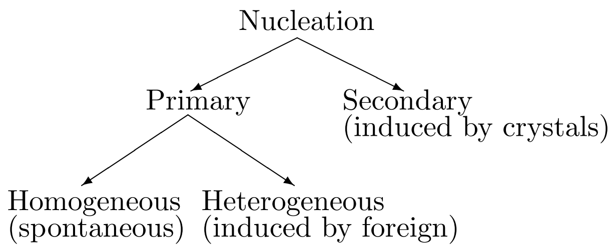

The formation of the nucleus leads to a Gibbs free energy.

Considering the interaction between solute and substrate in terms of the contact angle that the nucleus forms with the substrate, the reduction of the activation energy is given by the equation [1]–[2]:

$$\Delta G_{heterogeneous} = \omega(\theta).\Delta G_{homegeneous}, \tag{1}$$

where

$$\omega(\theta) = \frac{1}{4}(2+\cos\theta)(1-\cos\theta)^2 \tag{2}$$

or $\omega(\theta) = \dfrac{1}{2} - \dfrac{3}{4}\cos\theta + \dfrac{1}{4}\cos^3\theta$.

Numerical factor $\omega(\theta)$ has values between 0 and 1. The factor $\omega(\theta)$ in equation (1) is called Volmer's activation function.

Experimental test of the Volmer theory of heterogeneous nucleation can be found in [7].

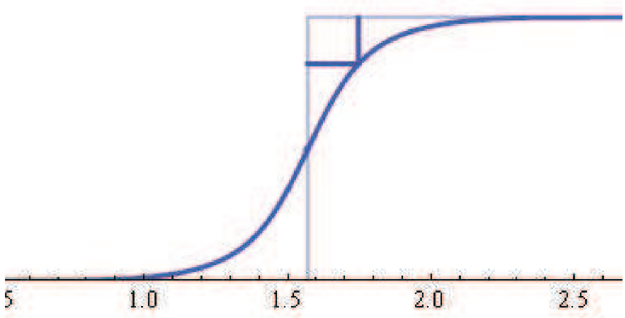

Figure 1: Reduction in free energy of the nucleation barrier due to heterogeneous nucleation as a function of the contact angle with the substrate [6], [18]

In the particular case of crystal clusters the factor $\omega(\theta)$ is modified by Kaishew [9].

Often in literature the function (2) occurs as function of Volmer–Weber–Kaishew.

For other results, see Kaishew [8], Mutaffschiev [10], Miloshev and Krastanov [11].

The Volmer theory is correct in predicting a dependence of critical supersaturation on contact angle in heterogeneous nucleation.

2. Preliminaries

Definition 1. *The (basic) step function is:*

$$\tilde{h}(t) = \begin{cases} 0, & \text{if} \quad t < \dfrac{\pi}{2}, \\ 1/2, & \text{if} \quad t = \dfrac{\pi}{2}, \\ 1, & \text{if} \quad t > \dfrac{\pi}{2}, \end{cases} \tag{3}$$

usually known as shifted Heaviside function.

Definition 2. ([16], [17]) *The Hausdorff distance (the H–distance)* [16] $\rho(f, g)$ *between two interval functions f, g on $\Omega \subseteq \mathbb{R}$, is the distance between their completed graphs $F(f)$ and $F(g)$ considered as closed subsets of $\Omega \times \mathbb{R}$.*

More precisely,

$$\rho(f, g) = \max\{ \sup_{A \in F(f)} \inf_{B \in F(g)} \|A - B\|, \sup_{B \in F(g)} \inf_{A \in F(f)} \|A - B\|\}, \tag{4}$$

wherein $\|.\|$ is any norm in $\mathbb{R}^2$, e. g. the maximum norm $\|(t, x)\| = \max\{|t|, |x|\}$; hence the distance between the points $A = (t_A, x_A)$, $B = (t_B, x_B)$ in $\mathbb{R}^2$ is $\|A - B\| = \max(|t_A - t_B|, |x_A - x_B|)$.

Let us point out that the Hausdorff distance is a natural measuring criteria for the approximation of bounded discontinuous functions.

3. Main results

In this Section we construct the following family of recurrence generated parametric functions based on Volmer–Weber–Kaishew activation function $\omega(\theta)$ (2):

$$\begin{aligned} W_i(t) &= (1+\lambda)\omega_i(t) - \lambda\omega_i^2(t), \\ \omega_{i+1}(t) &= \frac{1}{4}\left(2+\cos\left(t-\frac{1}{2}+\omega_i(t)\right)\right)\left(1-\cos\left(t-\frac{1}{2}+\omega_i(t)\right)\right)^2, \\ & \quad i=0,1,2,\ldots, \quad |\lambda|\le 1 \end{aligned} \tag{5}$$

with

$$\omega_0(t) = \frac{1}{4}(2+\cos t)(1-\cos t)^2; \quad \omega_0\left(\frac{\pi}{2}\right) = \frac{1}{2}. \tag{6}$$

Evidently, $\omega_i\left(\frac{\pi}{2}\right) = \frac{1}{2}$ and $W_i\left(\frac{\pi}{2}\right) = \frac{1}{2} - \frac{\lambda}{4}$ for $i = 0, 1, 2, \ldots,$.

The recurrence generated functions $W_0(t)$, $W_1(t)$, $W_2(t)$ and $W_3(t)$ are visualized on Fig. 2 – Fig. 3 for various λ.

In the special case $i = 0$ we have

$$W_0''(t) = -\frac{9}{8}\sin^2 t\left(2\lambda\cos^4 t - 5\lambda\cos^2 t - 2\cos t + \lambda\right). \tag{7}$$

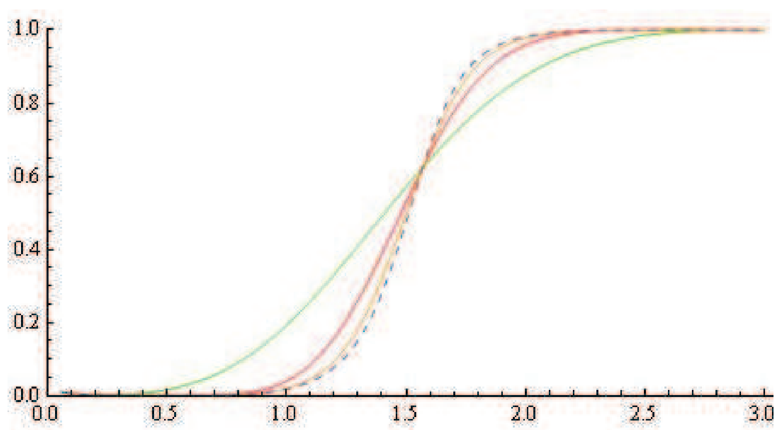

Figure 2: The graphics of recurrence generated functions for $\lambda = 0.5$: W_0 (green), W_1 (red), W_2 (orange) and W_3 (dashed). The reduction in free energy

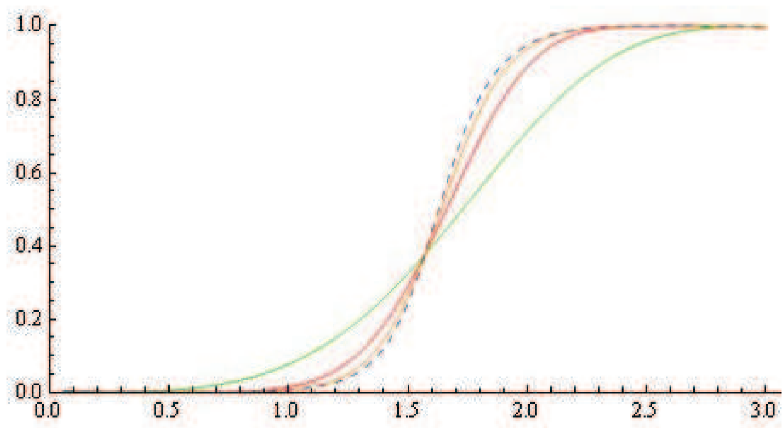

Figure 3: The graphics of recurrence generated functions for $\lambda = -0.5$: W_0 (green), W_1 (red), W_2 (orange) and W_3 (dashed). The reduction in free energy

From (7) we find that $W_0(t)$ has an inflection at point t^*, where t^* is the appropriate solution of the equation:

$$2\lambda \cos^4 t - 5\lambda \cos^2 t - 2\cos t + \lambda = 0. \tag{8}$$

3.1. The generalized cut function associated to the $W_0(t)$

The associate to the $W_0(t)$ cut function $C(t)$ is defined by

$$C(t) = \begin{cases} 0, & \text{if} \quad t < t_1, \\ W_0'(t^*)(t - t^*) + W_0(t^*), & \text{if} \quad t_1 \le t < t_2, \\ 1, & \text{if} \quad t \ge t_2. \end{cases} \tag{9}$$

3.2. Approximation of the cut function (9) by function $W_0(t)$

We next focus on the approximation of the cut function $C(t)$ by function $W_0(t)$.

Note that the slope of the function $C(t)$ on the interval $\Delta = [t_1, t_2]$ is $W_0'(t^*)$.

The straight line $y = W_0'(t^*)(t - t^*) + W_0(t^*)$ cross the lines $y = 0$ and $y = 1$ at the points t_1 and t_2 respectively.

Then, noticing that the largest uniform distance ρ between the cut $C(t)$ and $W_0(t)$ functions is achieved at the endpoints of the underlying interval Δ we have the following

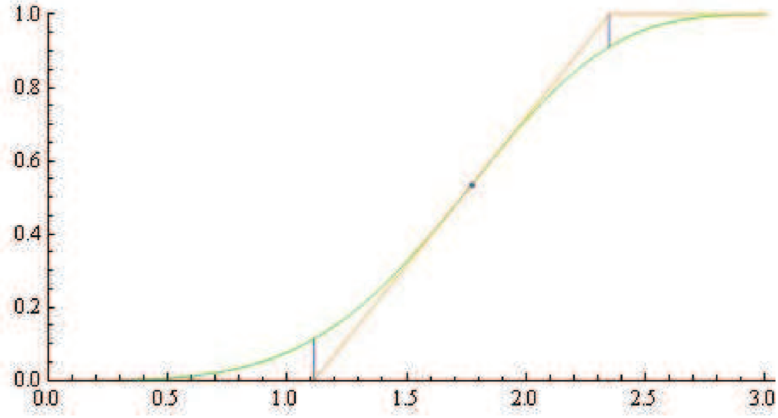

Figure 4: The cut and the $W_0(t)$ functions with $\lambda = -0.5$, $t^* = 1.7727$, $t_1 = 1.11284$, $t_2 = 2.34762$, $W_0(t_1) = 0.113062$, $W_0(t_2) = 0.91128$, uniform distance $\rho = 0.113062$

Theorem 3. *The function $W_0(t)$:*

i) is the function of best uniform approximation to function $C(t)$ in the interval Δ;

ii) approximates the cut function $C(t)$ in uniform metric with an error

$$\rho = \max\{W_0(t_1), 1 - W_0(t_2)\}. \tag{10}$$

In [18] Kyurkchiev consider the following family of recurrence generated functions:

$$\omega_{i+1}(t) = \frac{1}{4}\left(2 + \cos\left(t - \frac{1}{2} + \omega_i(t)\right)\right)\left(1 - \cos\left(t - \frac{1}{2} + \omega_i(t)\right)\right)^2, \quad i = 0, 1, 2, \ldots, \tag{11}$$

with

$$\omega_0(t) = \frac{1}{4}(2 + \cos t)(1 - \cos t)^2; \quad \omega_0\left(\frac{\pi}{2}\right) = \frac{1}{2}. \tag{12}$$

Evidently, $\omega_{i+1}\left(\frac{\pi}{2}\right) = \frac{1}{2}$ for $i = 0, 1, 2, \ldots,$.

The recurrence generated functions $\omega_0(t)$, $\omega_1(t)$, $\omega_2(t)$ and $\omega_3(t)$ are visualized on Fig. 5.

Denote the number of recurrences by p.

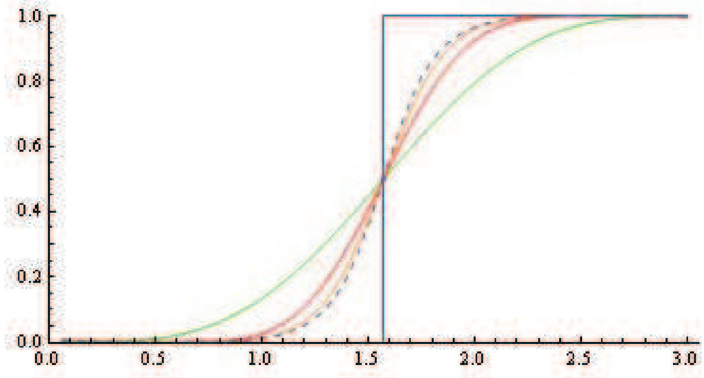

Figure 5: Approximation of the $\tilde{h}(t)$ by family (11) (resp. (5) for $\lambda = 0$) ; The graphics of recurrence generated functions: ω_0 (green), ω_1 (red), ω_2 (orange) and ω_3 (dashed); Hausdorff distance: $d_0 = 0.290832$, $d_1 = 0.226927$, $d_2 = 0.198579$, $d_3 = 0.184225$. The reduction in free energy

The following Theorem gives upper and lower bounds for d_p – the Hausdorff approximation of the shifted Heaviside function by means of this family.

Theorem 4. ([18]) *For given p, the H-distance d_p between the $\tilde{h}$ and the function ω_p the following inequalities hold:*

(13)
$$d_{l_p} = \frac{1}{1.5 \times \frac{\gamma_p}{2^{2p+1}}} < d_p < \frac{\ln\left(1.5 \times \frac{\gamma_p}{2^{2p+1}}\right)}{1.5 \times \frac{\gamma_p}{2^{2p+1}}} = d_{r_p}$$

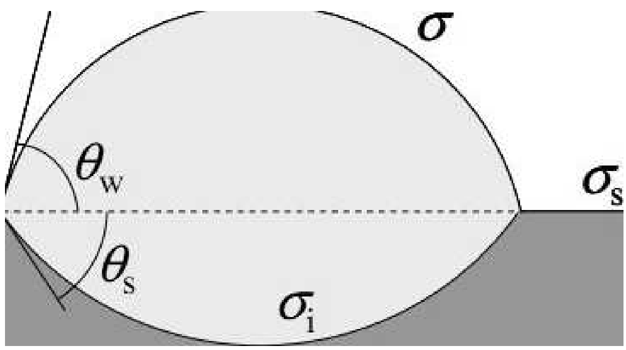

Figure 6: The lens-shaped geometry [14]

where

$$(14)\qquad \begin{aligned} \gamma_p &= 4\gamma_{p-1} + 3^{p+1},\ \ p = 1, 2, \ldots, \\ \gamma_0 &= 7. \end{aligned}$$

In the case of lens-shaped nuclei (see Fig. 6), the lens volume is expressed as [12]:

$$(15)\qquad \frac{V_n}{4/3\pi R^3} = \omega(\theta_w) + \left(\frac{\sin\theta_w}{\sin\theta_s}\right)^3 \omega(\theta_s) = F(\theta_w, \theta_s)$$

where $\omega(\theta_w)$ and $\omega(\theta_s)$ are given by (2). The factor $F(\theta_w, \theta_s)$ depend on the two angles θ_w and θ_w.

The factors $\omega(\theta_w)$, $\omega(\theta_s)$ and $F(\theta_w, \theta_s)$ are visualized on Fig. 7–Fig. 8.

4. Conclusion

A family of recurrence generated parametric functions based on Volmer–Weber–Kaishew activation function is introduced finding application in nucleation theory, geophysics and neural network theory.

In this note we consider dependence of supersaturation on contact angle by means of this family.

Numerical examples, illustrating our results are given.

We propose the following model:

$$\frac{\Delta G^i_{heterogeneous}}{\Delta G^i_{homegeneous}} = W_i(t);\ \ i = 0, 1, 2, \ldots$$

For $i = 0$ we have the classical Volmer–Weber–Kaishew equation for the nucleation rate (1).

Certain interest is the reduction in free energy of the nucleation barrier due to heterogeneous nucleation as a function of the contact angle with the substrate.

From the Fig. 2–Fig. 3 it can be seen that the “supersaturation” is fast.

We propose a software module (intellectual property) within the programming environment *CAS Mathematica* for the analysis of the considered family of recurrence generated (VWKAF) functions.

The module offers the following possibilities:

– generation of the activation functions under user defined value of the number of recursions p and parameter λ;

– calculation of the uniform distance ρ, between the function $C(t)$ and the functions $W_i(t)$;

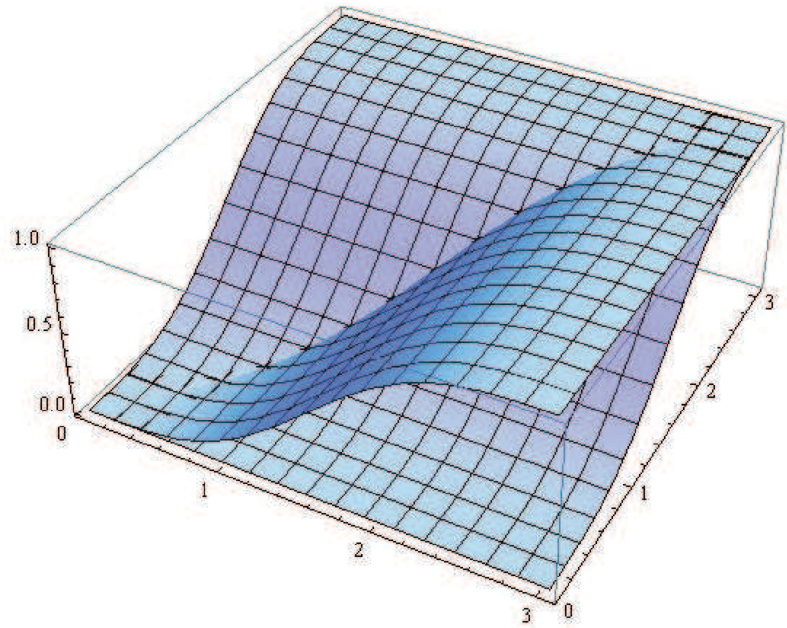

Figure 7: The factors $\omega(\theta_w)$ and $\omega(\theta_s)$

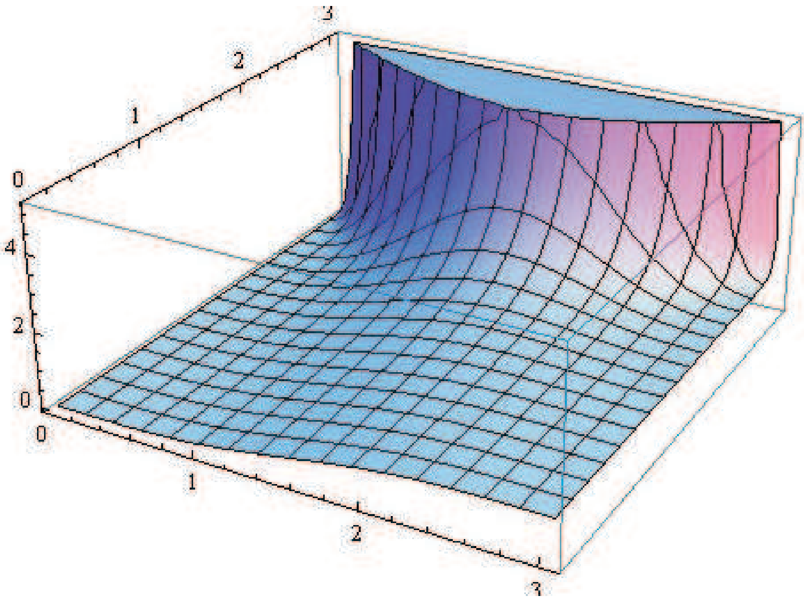

Figure 8: The factor $F(\theta_w, \theta_s)$

– software tools for animation and visualization.

I will explicitly say that the results have independent significance in the study of issues related to neural networks.

Some family of recurrence generated parametric activation functions is discussed from various approximation and modelling aspects in [19]–[27].

REFERENCES

[1] M. Volmer, A. Weber. Keimbildung in Übersättigten Gebilden. *Z. Physikal. Chemie (Leipzig)* **119** (1926), 277–301.

[2] M. Volmer. Kinetic der Phasenbildung. Steinkopf, Leipzig, 1939.

[3] R. Becker, W. Doring. Kinetische Behandlung der Keimbildung in Übersättigten Dämpfen. *Ann. Phys. (Leipzig)* **24** (1935), 719.

[4] J. Frenkel. A General Theory of Heterophase Fluctuations and Pretransition Phenomena. *J. Chem. Phys.* **7** (1939), 538–547.

[5] J. Zeldovich. On the theory of new phase formation. *Acta Physicochimica USSR* **18**, *1* (1943).

[6] J. Garcia–Ruiz. Nucleation of protein crystals. *Journal of Structural Biology* **142** (2003), 22–31.

[7] S. Twomey. Experimental test of the Volmer theory of heterogeneous nucleation. *J. Chem. Physics* **30**, *No 4* (1959), 941–943.

[8] R. Kaishew. *Bull. Acad. Bulg. Sci. (Phys.)* **1** (1950), 100.

[9] R. Kaishew. *Bull. Acad. Bulg. Sci. (Phys.)* **2** (1951), 191.

[10] B. Mutaffschiev. The Atomistic Nature of Crystal Growth. Springer, 1932.

[11] G. Miloshev, L. Krastanov. Influence of adsorption on the formation of embryo lunules. *Tellus XV* **3** (1963), 297–302.

[12] D. Kashchiev. Nucleation, Basic Theory with Applications. Butteworth–Heinemann, 2000.

[13] V. Dubrovskii. Nucleation Theory and Growth of Nanostructures. In: Nanoscience and Technology, Springer-Verlag, Berlin, Heidelberg, 2014.

[14] E. Clouet. Modeling of nucleation processes, In: Handbook **Vol. 22A**, Fundamentals of Modeling for metals processing (Eds D. Furrer and S. Semiatin), 2009, 203–219.

[15] L. Bentea, M. Watzky, R. Finke. Sigmoidal nucleation and growth curves across nature fit by the Finke-Watzky model of slow continuous nucleation and autocatalytic growth: Explicit formula for the lag and growth times plus other key insights. *J. Phys. Chem.* (2017), DOI:10.1021/acs.jpcc.6b12021

[16] F. Hausdorff Set Theory, 2nd ed., Chelsea Publ., New York, 1962.

[17] B. Sendov. Hausdorff Approximations. Kluwer, Boston, 1990.

[18] N. Kyurkchiev. A note on the Volmer's activation (VA) function. *Compt. rend. Acad. bulg. Sci.* **70**, *6* (2017), 769–776.

[19] N. Kyurkchiev. A family of recurrence generated sigmoidal functions based on the Verhulst logistic function. Some approximation and modeling aspects. *Biomath Communications* **3**, *2* (2016), DOI: http://dx.doi.org/10.11145/bmc.2016.12.171.

[20] N. Kyurkchiev, S. Markov. Hausdorff approximation of the sign function by a class of parametric activation functions. *Biomath Communications* **3**, *2* (2016), DOI: http://dx.doi.org/10.11145/bmc.2016.12.217.

[21] A. Iliev, N. Kyurkchiev, S. Markov. A family of recurrence generated parametric activation functions with application to neural networks. *Int. J. on Res. Inn. in Eng. Sci. and Techn. (IJRIEST)* **2** *1* (2017), 60–69.

[22] N. Kyurkchiev, A. Iliev, S. Markov. Families of recurrence generated three and four parametric activation functions. *Int. J. Sci. Res. and Development* **4**, *12* (2017), 746–750.

[23] V. Kyurkchiev, N. Kyurkchiev. Afamily of recurrence generated functions based on Half-hyperbolic tangent activation functions. *Biomedical Statistics and Informatics* **2**, *3* (2017), 87–94.

[24] V. Kyurkchiev, A. Iliev, N. Kyurkchiev. On some families of recurrence generated activation functions. *Int. J. of Sci. Eng. And Appl. Sci.* **3**, *3* (2017), 243–248.

[25] N. Kyurkchiev, S. Markov. On the Hausdorff distance between the Heaviside step function and Verhulst logistic function. *J. Math. Chem.* **54**, *1* (2016), 109–119.

[26] N. Kyurkchiev, A. Iliev, S. Markov. Some techniques for recurrence generating of activation finctions. LAP LAMBERT Academic Publishing, 2017, ISBN 978-3-330-33143-3.

[27] N. Kyurkchiev, S. Markov. Sigmoid functions: Some Approximation and Modelling Aspects. LAP LAMBERT Academic Publishing, Saarbrucken, 2015, ISBN 978-3-659-76045-7.

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