

Monte Carlo simulation of a nematic liquid crystal cell with a hemispheric defect on one electrode

C. BERLIC, E. BARNA, C. CIUCU*

Bucharest University, Department of Physics, Magurele, POBox MG 11 Magurele-Bucharest, Romania

We report Monte Carlo simulations of a liquid crystal cell having a small hemispherical defect on one of its electrodes. Using the Lebwohl-Lasher model, we obtained the order parameter for the bulk region and inside the cavity. We concluded that the confinement and the geometry of the system play a crucial role for the behavior of the local nematic director.

(Received November 26, 2007; accepted December 4, 2007)

Keywords: Nematic liquid crystals, Liquid crystals director, Order parameter, Monte Carlo simulation

Liquid crystals represent a state of matter whose characteristics are in-between those of an isotropic liquid and those of a solid crystal. They have properties such as the flowing characteristic to liquids, as well as the anisotropy of optical, electrical and magnetic phenomena characteristic to the crystalline state, which are due to the partial ordering of molecules [1]-[4]. Materials which exhibit one or more such mesophases are generally composed of molecules having a geometrical anisotropy, like line or disc shaped molecules [1], [4]. The molecular order is imposed either in a certain temperature range, which is the case of thermotropic liquid crystals, or in a given concentration range, in the case of lyotropic liquid crystals [4].

Liquid crystals constitute a class of materials which, due to their numerous applications in the fields of science and technology, have drawn the attention of scientists dealing with fundamental research [5]-[10], as well as those in applied physics [11]-[14].

It is well known that the main application of liquid crystals is that of display devices, due to the possibility of manipulation of the molecular director via magnetic and electrical fields, as well as by anchoring to the surface of contact [9]. Over the last decade, the focus of researches has been the problem of liquid crystals which are confined in various spherical or cylindrical structures, because of the superior application possibilities which ensue [5], [12], [13].

The orientational order of liquid crystals is possible due to the fact that molecule interactions are anisotropic, but this fact makes the task of theoretically describing this class of materials confined in various restrictive geometries much more difficult [15]. Several theories based on the phenomenological treatment of Frank [16], or on the minimization of the free energy [7] have been proposed, but all of them involve especially complex calculus, making the use of approximations necessary.

Another way of describing the orientational order and the properties of liquid crystals is by using computer simulations [17]-[22]. Among their well known advantages [23], one can mention: the ability to test proposed theories without using expensive equipment,

deducing parameters which are hard or even impossible to determine experimentally in ideal conditions, such as: the radial distribution function of liquids [24], the order parameter of liquid crystals [20], the radius of gyration of macromolecules [23], or performing a "computer experiment" in special physical conditions [25].

In this paper, we present the results of Monte Carlo simulations of a nematic liquid crystal cell having a small hemispherical defect on one electrode.

1. Method of study

Due to the unprecedented progress of computational techniques, especially as far as processing power and memory is concerned, but also of programming languages, computer simulations have become frequently used tools in physics, chemistry, mathematics or economy [24]. The Monte Carlo simulation was devised by von Neumann, Ulam and Metropolis in order to study the diffusion of neutrons in fissionable materials, and has since then been used on a wider and wider scale to study physical systems, including liquid crystals [23], [24], [26], [27].

The Monte Carlo simulation is achieved based on the method proposed by Metropolis [23], [24], [26]-[29], which has the advantage that, beside taking into account the thermal fluctuations of the system, also ensures the principle of ergodicity, according to which all states accessible to the thermodynamic system should be explored.

According to the before mentioned method, we assume that at a certain moment the system has the energy E_1 , and that it evolves towards a state characterized by an energy E_2 , with a probability of transition W . If the energy of the new state is smaller than that of the initial state, $\Delta E = E_2 - E_1 < 0$, then $W = 1$ and the new state is accepted, because it is favorable from an energetic point of view.

If $\Delta E > 0$, then the new state is accepted with a probability

$$W = e^{-\frac{\Delta E}{kT}} \quad (1)$$

where k is the Boltzmann constant and T is the temperature of the system.

In order to realize this requirement, a random number is generated, uniformly distributed in the interval $[0, 1]$ which is compared to the probability from equation (1). If it is smaller than W , then the new state is accepted, and if not we consider that the system remains in the old state, which is once more added to the statistical average [24].

The order inside a liquid crystal cell is described by the order parameter S , which is defined in such a way as to describe the order of the system with respect to a preferential axis, and has the following characteristics [4]:

- Due to the molecular symmetry, the only angle necessary to describe the orientation of the molecule with respect to the preferential axis is the angle θ between the molecule and the axis, so $S=S(\theta)$;
- The order parameter has to have the value 1 in the case in which all liquid crystal molecules are oriented along the direction n , which is the case of perfect order.
- The order parameter must be equal to 0 in the case of an isotropic liquid, which is the case of disorder.
- Its values must range between 1 and 0, depending on the extent of order of the molecules, for all intermediate states.

The expression which satisfies these requirements is

$$S = \langle P_2(\cos\theta) \rangle = \frac{3\langle \cos^2\theta \rangle - 1}{2} \quad (2)$$

where $P_2(\cos\theta)$ is the Legendre polynomial of order 2, and $\langle \rangle$ is the statistical average [1], [2], [4].

The order parameter of liquid crystals plays a central role in all theoretical and experimental inquiries regarding their behavior.

A special problem arises in the case of the computer simulations, because, in the absence of an external electric or magnetic field, or in the absence of walls which dictate the orientation of molecules, one cannot know during the simulation, which is the preferential axis with respect to which the molecules orient themselves [23].

For this reason, the orientation of a molecule is given through the cartesian components of a versor $\vec{e} = (e_x, e_y, e_z)$, and a tensor order parameter is defined:

$$Q_{\alpha\beta} = \frac{3}{2} \left(e_\alpha e_\beta - \frac{1}{3} \delta_{\alpha\beta} \right) \quad (3)$$

where $\delta_{\alpha\beta}$ is the Kronecker symbol [1], [2], [20], [23].

From the way in which it is defined, it is noticeable that the tensor order parameter has two important properties: it is a symmetric tensor, $Q_{\alpha\beta} = Q_{\beta\alpha}$, and it has a

zero trace, $Q_{xx} + Q_{yy} + Q_{zz} = 0$, meaning that only 5 of its components are independent.

By solving the eigenvalue eigenvector problem for the tensor Q , we find that the biggest eigenvalue is the order parameter S , and the corresponding eigenvector is the direction \vec{n} [20], [23].

In the investigation through Monte Carlo simulations of nematic liquid crystal cells, the Lebwohl – Lasher model [30], [31] is widely used, model which was introduced over three decades ago and that has been used since then, especially in the study of the nematic liquid crystals in complex geometries [17]-[22].

According to this model, the liquid crystal molecules are considered as unit vectors (versors or spins), which occupy fixed positions in the sites of a cubic crystalline lattice.

These versors are free to rotate in space and interact with each other through an orientation dependent energy. The fact that the molecules' centers of mass are arranged in an ordered fashion does not contradict the fact that in a liquid crystal there is no position order of the molecules, because, in a real liquid crystal, the molecules arrange themselves in ordered domains; in fact, each spin represents an ordered domain encompassing many molecules whose centers of mass are disordered distributed [20].

The interaction energy between two such spins is [20]:

$$E_{ij} = \begin{cases} 0 & , \text{if the spins are not first neighbours} \\ -\varepsilon \cdot P_2(\cos\theta_{ij}) & , \text{otherwise} \end{cases} \quad (4)$$

where ε describes the strength of interaction between the two spins, P_2 is the second order Legendre polynomial, and θ_{ij} is the angle between the two spins.

The simulation results obtained following the Lebwohl – Lasher model are very close to the experimental data [15]: for temperatures below a reduced

critical temperature $T_{NI}^* = \frac{kT}{\varepsilon} = 1.1232$, the order

parameter has nonzero values, indicating that the state of the system is ordered (liquid crystal). Also, the jump in system energy indicates that the phase transition between a liquid crystal and an isotropic liquid is a first order one, in agreement with experimental data. The value of the order parameter which was found using this model is $S = 0.7$, and is also in good agreement with the experimental data.

2. Results and discussion

The nematic liquid crystal cell used in the simulation is of rectangular shape, having the dimensions $L \times L \times H$, and in its lower electrode there is a small hemispheric defect of radius R , as shown in Fig. 1. The presence of this defect makes it much harder to describe the order of the system inside the cell, as well as in the cavity, where the effects of confinement become important. This system is however interesting to study both from a theoretical and

from an experimental point of view, given its modern applications in display systems [32]-[43].

In order to avoid boundary effects, periodic boundary conditions were used along the X and Y directions [23], [24], [26].

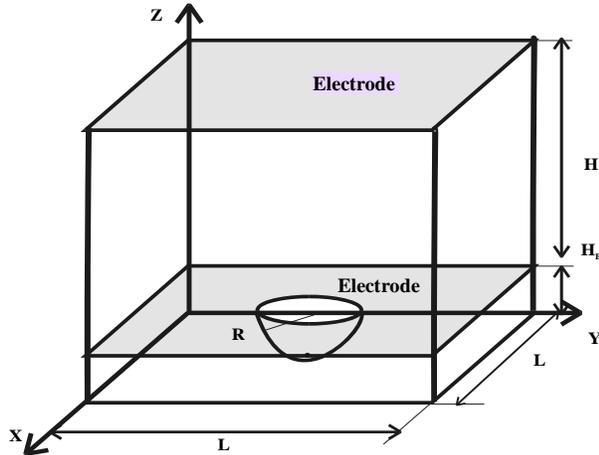


Fig. 1. The geometry of the simulated liquid crystal cell.

The spins which are not placed in the immediate vicinity of the walls interact with each other through a reduced energy $\varepsilon_B = 1$ and are free to rotate inside their cells following a standard Monte Carlo procedure: a random spin is chosen and the interaction energy with its first neighbors is computed. This spin rotates randomly with a small angle, following the described procedure [26], and then the interaction energy for the new state is computed. This new state is accepted according to the Metropolis criterion.

The anchoring of the molecules to the walls is realized by introducing fixed spins [17], [20]. These cannot rotate, but can interact with free spins through an energy ε_{SURF} . The orientation imposed by the walls is perpendicular to them, which in the case of the hemisphere means on the direction of the centre, as shown in Fig. 2.

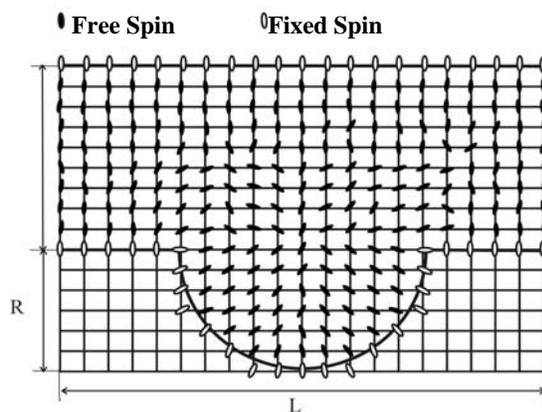


Fig. 2. Transversal section through the simulated cell, showing the free and fixed spins.

At temperatures below that of the nematic – isotropic phase transition, in the bulk, the spins would align themselves along the OZ axis, as imposed by the walls of the cell. Due to the presence of the cavity, especially above it, the molecular field is distorted, and a competition appears between the tendency to orient along the OZ axis and toward the centre of the hemisphere. It is obvious that under these conditions the order of the system must be described locally, which means that tensor order parameter defined in relation (2) is computed with the aid of the relation:

$$Q_{\alpha\beta} = \frac{1}{n_{spin}} \sum_{k=1}^{n_{spin}} \left(\frac{3}{2} \langle \varepsilon_{k\alpha} \varepsilon_{k\beta} \rangle - \frac{1}{2} \delta_{\alpha\beta} \right) \quad (5)$$

where n_{spin} is the number of spins which are averaged, and $\langle \rangle$ means the average over the statistic ensemble, [20]. If $n_{spin}=1$, then the average is performed solely on the statistic ensemble and describes the local order of the system.

A series of Monte Carlo simulations were performed on a cell having the dimensions $L \times L \times H = 20 \times 20 \times 14$ in lattice units, the radius of the defect being $R = 6.5$. The temperature chosen in the simulation was $T^* = 0.9$, which is pretty deep inside the nematic phase. The interaction energy between a free spin and a fixed one was $\varepsilon_S = 0.5 \varepsilon_B$, which corresponds to a relatively weak anchoring regime.

The results of the simulations showed that, for regions which are not in the immediate vicinity of the lower electrode having the defect, the order parameter obtained with the aid of the relation (5) is $S \cong 0.7$, value which corresponds to the well known results of the Lebwohl – Lasher model. However, the situation drastically changes for regions inside the hemispheric defect or in its immediate vicinity, where the order parameter exhibits significant variations from point to point, corresponding to the rotation of the molecular director, as was revealed through the study of the off diagonal components of the tensor $Q_{\alpha\beta}$.

In order to overcome these difficulties, other order parameters have historically been used, more suited to such a complicated geometry of the simulated system [17]. These are:

- The radial order parameter which describes the orientation of molecules on the direction of the centre of the cavity:

$$P_2^{RADIAL} = P_2(\vec{e} \cdot \vec{r}) \quad (6)$$

where \vec{e} is the spin attached to the molecule, and \vec{r} is the direction toward the centre of the cavity.

- The normal order parameter, which describes the orientation of molecules along the OZ axis, normal to the walls of the cell:

$$P_2^{NORMAL} = P_2(\vec{e} \cdot \vec{z}) \quad (7)$$

where \vec{z} is the unit vector of the OZ axis.

Due to geometrical reasons, P_2^{RADIAL} is much more relevant inside the cavity or in its immediate vicinity, while outside it P_2^{NORMAL} is much more useful in order to describe the order in the rest of the cell.

Fig. 3 shows the normal order parameter, in a horizontal plane located in the immediate vicinity of the lower electrode.

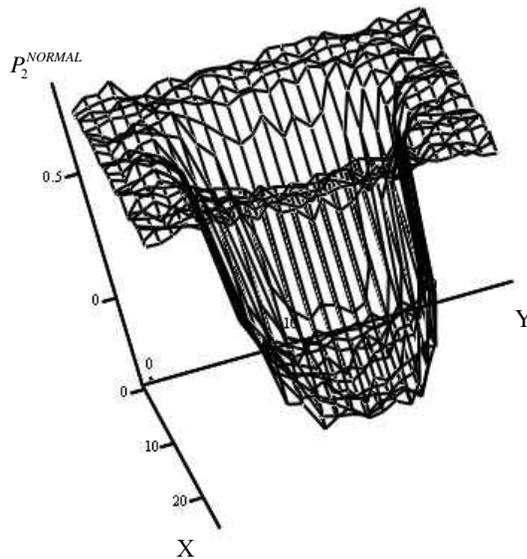


Fig. 3. The normal order parameter in a horizontal plane situated at $z=8$, for an anchoring energy $\epsilon_S = 0.5 \epsilon_B$ at the temperature $T^* = 0.9$.

By analyzing the behavior of P_2^{NORMAL} , it follows that for points which are not situated above the cavity, the order parameter has a high value, which means an orientation perpendicular to the walls, imposed by the electrodes. Above the cavity however, the parameter drops to negative values, suggesting the arrangement of molecules on a radial direction, the influence of the cavity being much more important in this case.

In order to decide if this “upside down hat” effect is due to the values used for the anchoring energy, another set of simulations was carried out, at a higher energy $\epsilon_S = 1.2 \epsilon_B$, the results being the similar.

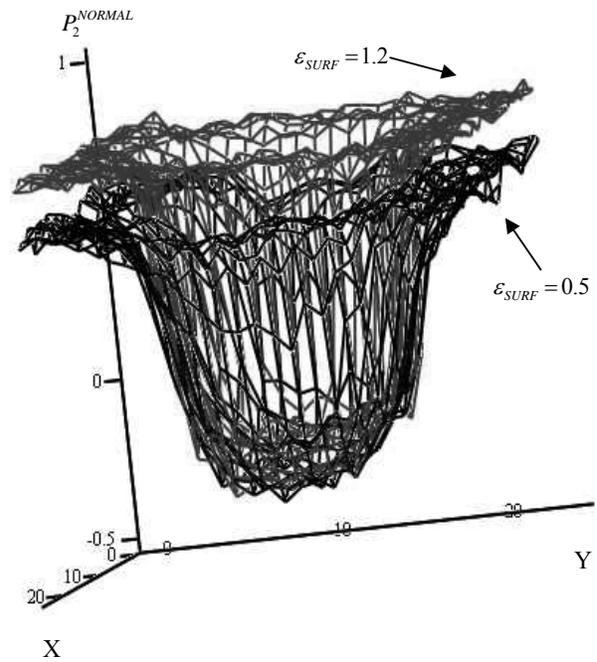


Fig. 4. Comparison between the values of the normal order parameter for two anchoring energies, $\epsilon_S = 0.5 \epsilon_B$ and $\epsilon_S = 1.2 \epsilon_B$, for $z = 8$ at the temperature $T^* = 0.9$.

By analyzing the graphs in Fig. 4 one can notice that the effect of the small anchoring energy is not of great importance, since the same dependence was observed for higher energies. Thusly, the shape of the “upside down hat” dependency is preserved, as in the case of lower energies, the values being somewhat greater outside the cavity. The fact that above the cavity the values of P_2^{NORMAL} are approximately the same suggests that the geometric effect induced by the shape of the surface is predominant in that region.

Inside the cavity, due to its relatively small dimensions, the order is very good, leading to values of P_2^{RADIAL} close to 0.7 in both cases.

Truly remarkable is the fact that the effect of the cavity is maintained, if weaker, at temperatures higher than the nematic – isotropic transition temperature of the Lebwohl – Lasher model. Another set of simulations was therefore performed, at the reduced temperature $T^* = 1.3$, which is above the value $T_{NI}^* = 1.1232$, the results obtained for P_2^{NORMAL} being shown in Fig. 5.

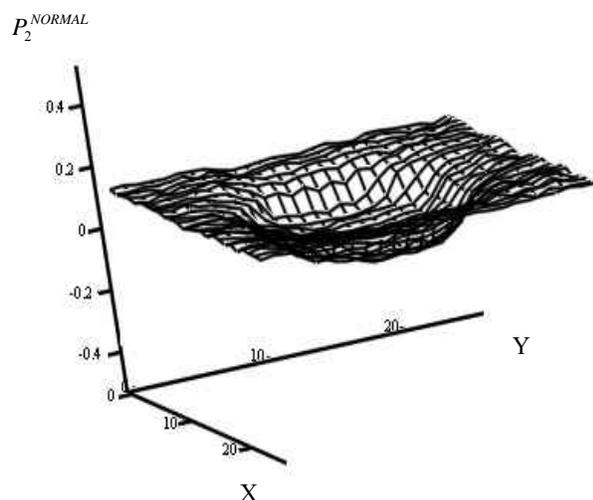


Fig. 5. The normal order parameter in a horizontal plane situated at $z=8$, for an anchoring energy $\varepsilon_S = 0.5 \varepsilon_B$, at a temperature $T^* = 1.2$, higher than the nematic – isotropic transition temperature.

The analysis of Fig. 5 shows that the effect of the cavity on the orientation of the molecules is maintained at temperatures above that of the nematic – isotropic transition, in which the spins situated above the cavity tend to orient themselves radially. It should be mentioned however that the effect is relatively weak and manifests itself only in the vicinity of the defect.

3. Conclusions

Computer simulations prove to be a valuable tool for investigating the properties of systems which seem impossible to predict using exact theoretical relations.

By using a special geometry of the nematic liquid crystal cell, it has been noticed that the order parameter of the system is strongly influenced by the presence of the cavity, its graph having a special “upside down hat” shape, which is valid for low anchoring energies as well as high ones.

Thusly it was deduced that confinement and the geometry of the system play a central role in determining the orientation of the liquid crystal molecules, fact which may lead to new perspectives in top applicative domains related to liquid crystal display systems.

References

- [1] P. G. de Gennes, Clarendon Press, Oxford, 1974.
- [2] S. Chandrasekhar, Nauka, Moscow, 1978.
- [3] E. B. Priestley, P. J. Wojtowicz, K. Sheng, Plenum Press, New York, 1975.
- [4] L. Georgescu, V. Popa-Niță, E. Barna, C. Berlic, "Fizica Cristalelor Lichide. Aplicații", Ed. Universității din București, București, 2002.
- [5] S. Kralj, S. Zumer, Phys. Rev. E, **51**(1), 366 (1995).
- [6] A. Th. Ionescu, E. Barna, G. Barbero, A. L. Alexe-Ionescu, Phys. Rev. E, **65**, 041710 (2002).
- [7] V. Popa-Niță, S. Kralj, Phys. Rev. E **73**, 041705 (2006).
- [8] S. Beslagic, I. Gerlic, S. Kralj, V. Popa-Niță, Mol. Cryst. Liq. Cryst. **449**, 135 (2006).
- [9] A. L. Alexe-Ionescu, A. Th. Ionescu, E. Barna, N. Scaramuzza, G. Strangi, J. Phys. Chem. B, **107**, 5487 (2003).
- [10] A. L. Ionescu, A. Ionescu, E. S. Barna, V. Barna, N. Scaramuzza, J. Phys. Chem. B, **108**, 8894 (2004).
- [11] V. Barna, R. Caputo, A. de Luca, N. Scaramuzza, G. Strangi, C. Versace, C. Umeton, R. Bartolino, G. N. Price, Optics Express **14**, 7 (2006).
- [12] G. Strangi, S. Ferjani, V. Barna, A. de Luca, N. Scaramuzza, C. Versace, C. Umeton, R. Bartolino, Optics Express, **14**, 17 (2006).
- [13] G. Strangi, V. Barna, R. Caputo, A. de Luca, C. Versace, N. Scaramuzza, C. Umeton, R. Bartolino, G. N. Price, Phys. Rev. Lett. **94**, 063903 (2005).
- [14] A. L. Ionescu, A. Ionescu, E. S. Barna, V. Barna, N. Scaramuzza, Appl. Phys. Lett. **84**(1), 40-42 (2004).
- [15] J. A. M. Ilnytskyi, J. Phys. Stud. **1**, 2 (1997).
- [16] F. C. Frank, Discuss. Faraday. Soc. **25**, 19 (1958).
- [17] A. M. Smondyrev, A. Pelcovits, Liq. Cryst. **26**, 2 (1999).
- [18] C. Chiccoli, S. Guzzetti, P. Pasini, C. Zannoni, Mol. Cryst. Liq. Cryst. **360** (2001).
- [19] E. Berggren, C. Zannoni, C. Chiccoli, P. Pasini, F. Semeria, Int. J. Modern Phys. C **6**, 1 (1995).
- [20] N. Scaramuzza, C. Berlic, E. S. Barna, G. Strangi, V. Barna, A. Th. Ionescu, J. Phys. Chem. B **108**, 3207 (2004).
- [21] E. Berggren, C. Zannoni, C. Chiccoli, P. Pasini, F. Semeria, Phys. Rev. E **49**, 1 (1994).
- [22] C. Chiccoli, P. Pasini, C. Zannoni, Physica A, **148**, (1998).
- [23] M. P. Allen, D. J. Tildesley, "Computer Simulation of Liquids", Oxford University Press, 1989.
- [24] L. Georgescu, L. M. Constantinescu, E. Barna, C. Miron, C. Berlic, "Introducere în fizica polimerilor", Ed. Credis, București, 2004.
- [25] I. Stamatina, C. Berlic, A. Vaseashta, Thin Solid Films **495**, 1-2 (2006).
- [26] D. Frenkel, B. Smit, "Understanding Molecular Simulations. From Algorithm to Applications.", Academic Press, New York, 2002.
- [27] D. P. Landau, K. Binder, "A Guide to Monte Carlo Simulations in Statistical Physics", Cambridge University Press, 2000.
- [28] N. Metropolis, A. N. Rosenbluth, M. N. Rosenbluth, A. H. Teller, E. Teller, J. Chem. Phys. **21**, 1087 (1953).
- [29] C. Berlic, L. M. Constantinescu, Revista de Chimie

- 55**, 11 (2004).
- [30] G. Lasher, Phys. Rev. A **5**, 3 (1972).
- [31] P. A. Lebwohl, G. Lasher, Phys. Rev. A **6**, 1 (1972).
- [32] A. L. Ionescu, A. Th. Ionescu, E. S. Barna, V. Barna, N. Scaramuzza, Appl. Phys. Lett. **45**, (2003).
- [34] T.-Y. Yoon, J.-H. Park, J. Sim, S.-D. Lee, Appl. Phys. Lett. **81**, 13 (2002).
- [35] V. Barna, C. Miron, C. Berlic, E. S. Barna, Mat. Plastice **40**, 4 (2003).
- [36] G. P. Crawford, S. Zumer, Eds., "Liquid Crystals in Complex Geometries Formed by Polymer and Porous Networks", Taylor and Francis, London, 1996.
- [37] A. L. Ionescu, A. Th. Ionescu, E. S. Barna, V. Barna, N. Scaramuzza, J. Phys. Chem. B **10**, 26 (2004).
- [38] T. O. Cheche, E. S. Barna, Appl. Phys. Lett. **89**(4), 42116 (2006).
- [39] R. Bartolino, N. Scaramuzza, E. S. Barna, A. Th. Ionescu, L. A. Beresnev, L. M. Blinov, J. Appl. Phys. **84**(5), 2835 (1998).
- [40] E. S. Barna, C. Iliescu, C. Miron, V. Barna, Mat. Plastice, **41**(1), 36 (2004).
- [41] E. Gatin, C. Berlic, A. Popescu, E. S. Barna, Physica Medica, XVI, 1, 3 (2000).
- [42] R. Bartolino, N. Scaramuzza, D. E. Lucchetta, E. S. Barna, A. Th. Ionescu, L. M. Blinov, J. Appl. Phys. **85**(5), 2870 (1999).
- [43] A. L. Ionescu, G. Barbero, A. Th. Ionescu, E. S. Barna, Phys. Lett. A, **314**, 332 (2003).

*Corresponding author: cristian1st@hotmail.com