

Memory Effects in Randomly Perturbed Nematic Liquid Crystals

Amid Ranjkesh, Milan Ambrožič, and Samo Kralj

Abstract—We study the typical domain size and configuration character of a randomly perturbed system exhibiting continuous symmetry breaking. As a model system we use rod-like objects within a cubic lattice interacting via a Lebwohl–Lasher-type interaction. We describe their local direction with a headless unit director field. An example of such systems represents nematic LC or nanotubes. We further introduce impurities of concentration p , which impose the random anisotropy field-type disorder to directors. We study the domain-type pattern of molecules as a function of p , anchoring strength w between a neighboring director and impurity, temperature, history of samples. In simulations we quenched the directors either from the random or homogeneous initial configuration. Our results show that a history of system strongly influences: i) the average domain coherence length; and ii) the range of ordering in the system. In the random case the obtained order is always short ranged (SR). On the contrary, in the homogeneous case, SR is obtained only for strong enough anchoring and large enough concentration p . In other cases, the ordering is either of quasi long range (QLR) or of long range (LR). We further studied memory effects for the random initial configuration. With increasing external ordering field B either QLR or LR is realized.

Keywords—Lebwohl-Lasher model, liquid crystals, disorder, memory effect, orientational order.

I. INTRODUCTION

THE past decade has witnessed an increased interest in the study of two-component mixtures consisting of nanoparticles (NPs) in a host material [1]-[5]. A characteristic feature of a nanoparticle is that at least one of its dimensions is of the order of nanometers. Such systems are expected to play an important role in the emerging field of nanotechnology and also in composites with extraordinary material properties. These mixture can in general exhibit behaviors which are not encountered in either of isolated components, opening gates to new applications.

Our particular interest is cases where the host component is a soft material [6]. These materials can then exhibit relatively strong responses, even to local low-energy excitations. Typical representatives of soft materials, with great application potential, are various liquid crystals phases [6]. Their soft character is due to continuous symmetry breaking via which

Amid Ranjkesh is with the Faculty of Natural Sciences and Mathematics, University of Maribor, Koroška 160, 2000 Maribor, Slovenia, (phone: +386 2 22 93 844, e-mail: amid.ranjekesh@uni-mb.si).

Milan Ambrožič is with the Faculty of Natural Sciences and Mathematics, University of Maribor, Koroška 160, 2000 Maribor, Slovenia, (phone: +386 2 22 93 844, e-mail: milan.ambrozic@uni-mb.si).

Samo Kralj is with the Faculty of Natural Sciences and Mathematics, University of Maribor, Koroška 160, 2000 Maribor, Slovenia, (phone : +386 2 22 93 844, e-mail: samo.kralj@uni-mb.si) and the Condensed Matter Physics Department, Jožef Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia.

LC phases are reached, giving rise to Goldstone excitation modes. LCs are also optically anisotropic and transparent, their structure can be readily controlled by the confining surfaces and applying an external electric or magnetic field. LCs exhibit a rich pallet of different structures and phases that can display almost all physical phenomena. In addition the chemistry of LCs is relatively well developed; therefore the synthesis of LC molecules with the desired behavior can be achieved with a certain degree of ease. As a result of these properties, even pure LC systems have found several applications, in particular in the electro-optics industry.

We henceforth limit our attention to rod-like LC molecules and to thermotropic LCs in which liquid crystal phases are induced by lowering the temperature from the ordinary liquid (isotropic) phase. The nematic configuration represents the simplest liquid crystal phase [6]. In the bulk nematic phase LC molecules tend to be oriented homogeneously along a single symmetry breaking direction. At the mesoscopic level the average local orientational ordering is commonly described by the nematic director field \bar{n} . The directions $\pm\bar{n}$ of this unit vector field are physically equivalent, reflecting the so called head-to tail invariance of LC phase on the mesoscopic scale. If LCs are suddenly quenched from the isotropic to the lower symmetry nematic phase, then unavoidably a domain pattern forms [7]. The reason behind this is continuous symmetry breaking and causality (i.e., a finite speed with which information spreads in a system). Generality of this mechanism gives rise to a broad universality of the phenomenon. The basic features of domain pattern dynamics in a pure bulk are described by the Kibble-Zurek mechanism [8],[9]. It was originally introduced to explain the formation of topological defects in the early universe following the big bang [8]. For latter purposes we summarize main features of this universal mechanism for the case of isotropic-nematic (I-N) phase transition. In the I-N quench the continuous orientational symmetry is broken. A randomly chosen configuration of the symmetry breaking field \bar{n} is established in causally disconnected parts [7]. This choice is based on local fluctuation mediated preferences. Consequently a domain structure appears, which is well characterized by a single domain length ξ_d . At the domain walls topological defects forms. Such structure is energetically costly due to high concentration of domain walls and defects. To reduce these cost on average domain grow with time what is enabled by mutual annihilation of defects [10]-[11]. In the pure bulk system spatially homogeneous structure is gradually reached. However, if impurities are present, they can pin the defects [12]-[14]. Consequently, the domain structure can be stabilized.

In this contribution we study numerically a mixture of uniaxial nematic liquid crystals and rod-like NPs using a Lebwohl-Lasher [15],[16] lattice model. We consider cases where NPs and LC molecules tend to be oriented perpendicular to each other. We show that in such systems NPs induce strong biaxiality [17] in LC ordering. Furthermore, we show that NPs can stabilize domain pattern giving rise to short range ordering in the nematic LC phase [18],[19]. The plan of the paper is as follows. In the section II we present our model. The simulation results are presented and discussed in Sec. III. In the last section we summarize results.

II. MODEL

We consider an ensemble of $N \sim N_0^d$ cylindrically symmetrical particles within a lattice, where d stands for the dimensionality of the system. Neighboring sites are separated for a distance a_0 in a cubic cell of length $L=N_0a_0$. Local orientational ordering of a particle at the i -th site is given by a unit vector S_i , to which we henceforth refer as the ‘director’. We further set at randomly chosen sites of concentration p cylindrically symmetric quenched impurities enforcing orientational ordering along e_i . The orientations of impurities were randomly chosen without any preferred global orientation. We also imposed an homogeneous external (e.g. electric or magnetic) ordering field $B=B_{eB}$, which enforces orientational ordering along e_B . We considered systems exhibiting the so-called head-to-tail invariance, where $\langle S_i \rangle$ orientations are equivalent. This is characteristic for most LC molecules (where several structural details are averaged out via relatively fast molecular rotations) or nanotubes. With this in mind, we expressed the interaction energy of the system as [20].

$$f_{ijk} = -\frac{1}{2} \sum_{i,j} J_{ijk,n,n} (\bar{S}_i \cdot \bar{S}_j)^2 - \sum_i w_i (\bar{S}_i \cdot \bar{e}_i)^2 - B^2 \sum_i (\bar{S}_i \cdot \bar{e}_B)^2 \quad (1)$$

Here, $J > 0$ describes the ordering interaction among neighboring molecules tending to orient directors parallel or antiparallel. The sum over indices I runs over all the particles, and the indices j run over the first neighbors of the i th particle. At randomly chosen sites of concentration p , we placed impurities which are coupled with surrounding directors by the random anisotropy-type interaction of anchoring strength $w_i = w > 0$. At the remaining sites, we set $w_i = 0$. Our interest was to find the main structural characteristic of S_i patterns as a function of p , w and a history of such systems.

We described ordering in the three dimensional ($d=3$) Cartesian coordinate frame (x, y, z), whose axes point along unit vectors e_x, e_y and e_z , respectively. The external field is oriented along the x -axis, i.e. $e_B = e_x$.

In the 3D model we parameterize unit vectors S_i as :

$$s_i = e_x S_x^{(i)} + e_y S_y^{(i)} + e_z S_z^{(i)} \quad (2)$$

For convenience we scale quantities in Equation (1) with respect to J :

$$\tilde{B} = \frac{B}{\sqrt{J}} \quad \tilde{w}_i = \frac{w_i}{J} \quad \tilde{w} = \frac{w}{J}$$

We henceforth omit the tildes.

In simulations we either originated from randomly distributed orientations of directors, or from homogeneously aligned samples along a symmetry breaking direction. In the latter case, the directors are initially homogeneously aligned along e_x . We henceforth refer to these cases as the I) random and II) homogeneous case, respectively. The random case can be experimentally realized by quenching the system from the isotropic phase to the ordered phase without an external field (i.e. $B=0$). This can be achieved either via a sudden decrease of temperature or sudden increase of pressure. The homogeneous case can be realized by applying first a strong homogeneous external field B along a symmetry breaking direction. After a well enough alignment is achieved, the field is switched off. In order to diminish the influence of statistical variations we carried out several simulations (typically $N_{rep} \sim 10$) for a given set of parameters (i.e. w, p and a chosen initial condition).

The orientational ordering of the spin system can be characterized by the traceless symmetric order parameter tensor with 3×3 components:

$$Q_{mn} = \frac{3}{2} \langle S_{ijk,m} S_{ijk,n} \rangle - \frac{1}{2} I \quad (3)$$

where $S_{ijk,m}$ is the m -th component of the spin S_{ijk} . The brackets $\langle \dots \rangle$ denote the average of the quantity through the simulation cell. I is the identity matrix.

The correlation function measures both short- and long-range spin orientation ordering. It is defined in a manner analogous to the order parameter tensor:

$$G(r) = \frac{3}{2} \langle (\bar{S}_{ijk} \cdot \bar{S}_{mnl})^2 \rangle - \frac{1}{2} \quad (4)$$

where $\langle \dots \rangle$ is the average of the squares of the scalar products of only those spin pairs which are separated by distance r . We have calculated it numerically after relaxation of the spin system.

We fitted the correlation function to the following exponential form:

$$G(r) = (1-s) \exp\left(-\left(\frac{r}{\xi}\right)^m\right) + s \quad (5)$$

with three adjustable parameters: ξ , m and s . The coherence length ξ is roughly the average size of the domains around impurities. The parameter m measures the distribution width of coherence lengths if it deviates from the value 1. The last

parameter s measures the LC ordering on large scale: $s = 0$ indicates SRO while $s > 0$ indicates LRO or QLRO.

III. RESULTS AND DISCUSSION

Typical size of the lattice used in our calculations was $N^3=80$. We chose two specific values of anchoring strength, $W = 2$ and $W = 0.5$, and varied systematically impurity concentration P and temperature T^* . For specific value of P , we started simulations with some low temperature ($T^* = 0.1$), set the desired initial spin configuration and then gradually increased temperature. In these simulations there was no external field (except for considering very strong initial field to achieve aligned initial configuration, which is then turned off). We followed the evolution of the scalar order parameter S and the pair of the parameters s and ξ belonging to the correlation function (4) according to the form (5). Since both impurities and thermal fluctuations contribute to orientational disorder in the nematic phase, both parameters, S and s (which are strongly coupled to each other) are diminished when either impurity concentration or temperature is increased.

Moreover, we tested the system behavior upon increasing temperature according to four different scenarios relating to initial system configuration:

- Random initial orientation (complete disorder) of nematic spins at the lowest temperature ($T^* = 0.1$) followed by spins' relaxation. But for each higher temperature, the numerical procedure takes the last (relaxed) spin configuration of the previous (a little lower) temperature before relaxation at this temperature begins. We shortly denote this scenario by R (random).
- Random initial orientation for all temperatures, not only the lowest one. We shortly denote this scenario by RR (random-random).
- Homogeneous (in one direction) initial alignment (complete order) of nematic spins at the lowest temperature ($T^* = 0.1$) followed by spins' relaxation. But for each higher temperature, the numerical procedure takes the last (relaxed) spin configuration of the previous (a little lower) temperature before relaxation at this temperature begins. We shortly denote this scenario by H (homogeneous).
- Homogeneous initial orientation for all temperatures, not only the lowest one. We shortly denote this scenario by HH (homogeneous-homogeneous).

Experimentally scenario H means that the very strong homogeneous external field is used only in the beginning, at the lowest temperature, to align all spins. HH means that the initial spin configuration is aligned with the strong field for every temperature before spin relaxation. R means that the system is suddenly frozen from isotropic phase to the lowest temperature, and then the temperature is slowly increased. RR means the system is suddenly frozen from isotropic phase for every considered temperature before spin relaxation. The results are shown in Fig. 1-3.

The dependence of correlation length ξ on temperature, spin concentration and scenario is more interesting. It is evident

from Fig. 3 that the correlation length is not significantly different for the four scenarios, except for smaller values of impurity concentrations. But it can be noted that correlations length for R is systematically higher than for RR, while that for H is systematically higher than that for HH. Rearranging spins (either aligning or randomizing) for each temperature separately obviously lowers the correlation length a little. We show only the situation for $W = 2$ since the lines for $W = 0.5$ are much too irregular (large fluctuations) for the picture to be representative. It is evident from Fig. 3 already that the fluctuations in ξ are larger for smaller impurity concentrations. Averaging over several repetitions of the same temperature scan would smooth these curves but this requires much more computational time.

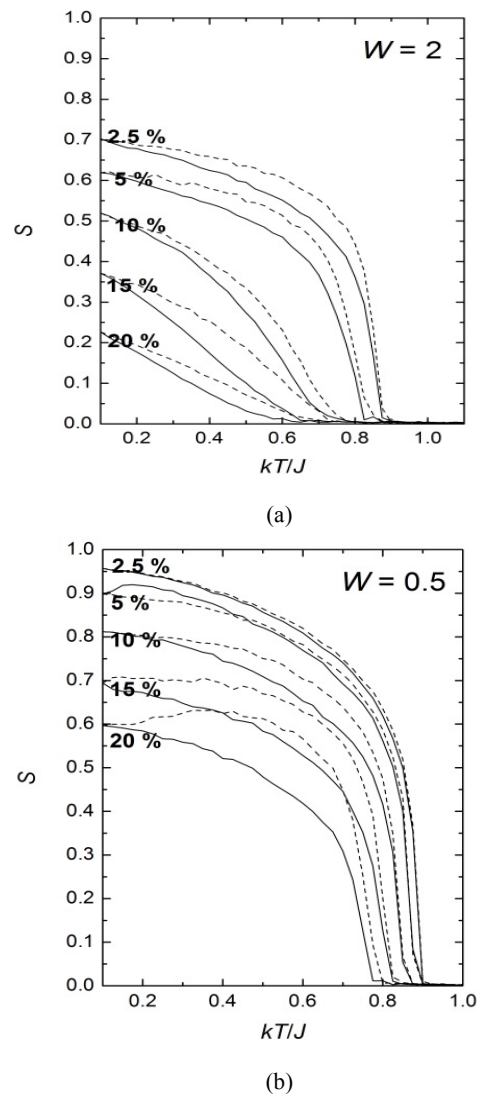
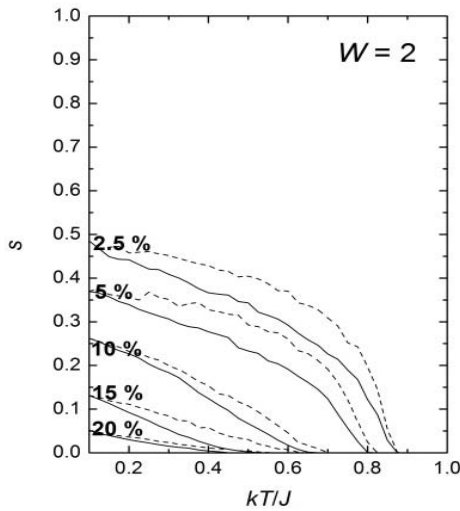
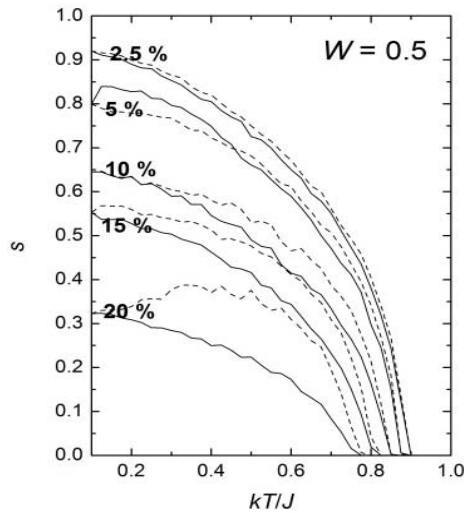


Fig. 1 Dependence of order parameter S on P (2.5 % to 20 %) and $T^* = kT/J$; $W = 2$ (a) and 0.5 (b). Scenarios: H (solid lines) and HH (dashed lines)



(a)



(b)

Fig. 2 Dependence of correlation function parameter s on P (2.5 % to 20 %) and T^* ; $W = 2$ (left) and 0.5 (right). Scenarios: H (solid lines) and HH (dashed lines)

We also noted that the parameter m is a decreasing function of temperature (Fig. 4). For low temperatures $m > 1$, while its value decreases below 1 (minimum) and approaches 1 again for temperatures above phase transition (where S goes to zero for H scenario, for instance).

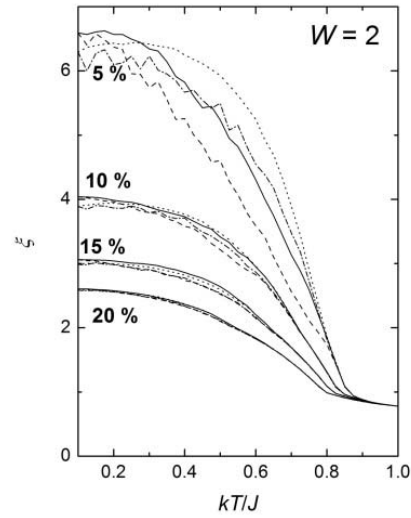


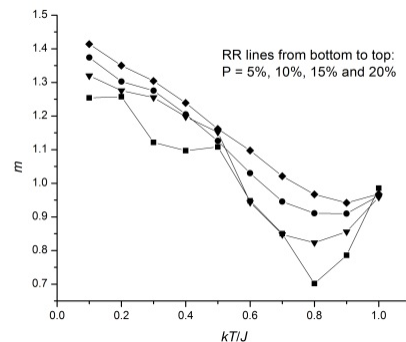
Fig. 3 Dependence of correlation length ξ on P (5 % to 20 %) and T^* ; $W = 2$. Scenarios: H (solid lines), HH (dashed lines), R (dotted lines) and RR (dash-dotted lines)

However, the explanation of this behavior of m is a little tricky and care is needed in the interpretation of results. The values of m different from 1 are usually assigned to some range of values of correlation length ξ about certain mean value. So, the correlation function can be written as composed of several simple exponential functions:

$$G(r) = (1 - s) \int f(\xi) \exp\left(-\frac{r}{\xi}\right) d\xi + s \quad (6)$$

With the normalized distribution $f(\xi)$ which is, of course, positive function. But different distributions f can explain only the case $m < 1$, and the form (5) of correlation function comes just approximately from (6). This is most easily seen from the fact that the sum (or integral) of convex functions $\exp(-r/\xi)$ of the variable r over the parameter ξ is again purely convex function of r corresponding to $m < 1$ in (5) while $m > 1$ gives a small concave part (for smaller values of r) of function (5).

The next problem is that in contrast to the parameters s and ξ the determination of parameter m through the fitting procedure is not so reliable.



(a)

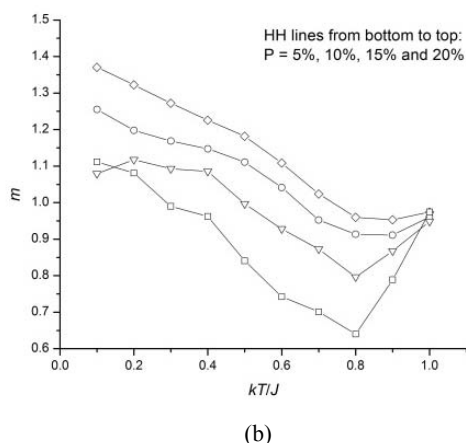


Fig. 4 Dependence of m on T^* ; $W = 2$, $P = 5\%$ to 20% ; RR (a) and HH (b) scenario

We also checked the influence of finite size N on the three parameters of correlation function. The first parameter, s , indicating the long-distance system order, has very small values, of the order of 0.01, even for small cubes, $N = 20$ or 30, while $s \sim 0.001$ for larger N . The fitting of the function (5) to s is thus rather unreliable, sometimes giving even negative values of s , so in these cases we simply locked the value $s = 0$, making fitting the parameters ξ and m more reliable. Indeed, the standard deviation of S and s (according to 8 values and not recalculated to theoretical standard deviation) is of the same order as mean values of S and s , themselves.

Fig.5 presents the dependence of correlation length on system size. For both free boundary and periodic boundary condition $\xi(N)$ is slightly increasing function of system size, and is larger for periodic boundary.

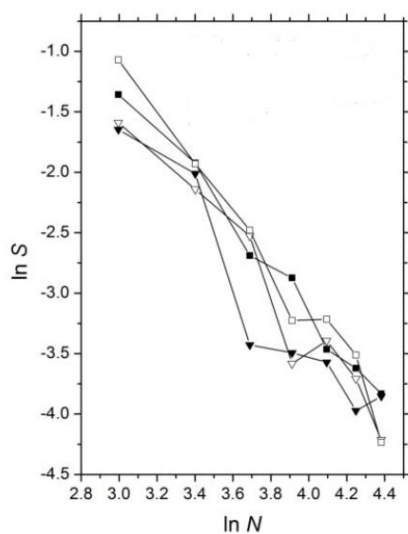


Fig. 5 Dependence of scalar order parameter S on the system size $p = 10\%$, $W = 2$, $kT/J = 0.1$ (\blacktriangle and \blacksquare) and $kT/J = 0.5$ (\square and \triangle) in periodic boundary (\square and \blacksquare) and free boundary (\triangle and \blacktriangle)

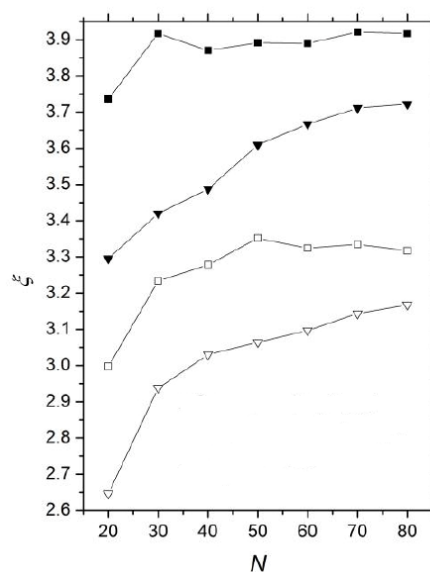


Fig. 6 Dependence of correlation length ξ on the system size $p = 10\%$, $W = 2$, $kT/J = 0.1$ (\blacktriangle and \blacksquare) and $kT/J = 0.5$ (\square and \triangle) in periodic boundary (\square and \blacksquare) and free boundary (\triangle and \blacktriangle)

We further analyzed how the domain-type ordering could be manipulated with external magnetic or electric ordering field. For this purpose we originated from the random initial configuration. We then applied an external field of strength B and calculated the configuration for different concentrations of impurities. Then the field was switched off and the configuration calculated again, to which we henceforth refer as the 'switch-off configuration'.

The corresponding calculated s is shown in Fig.7. From Fig. 7 it can be seen that the presence of external field develops QLRO or LRO (time-consuming finite size analysis to distinguish between the two cases was not carried out). This range of ordering remained as the field was switched off, although the correlation strength was reduced.

Note that above certain field strength the degree of ordering in the switch-off configuration is saturated becomes independent of B .

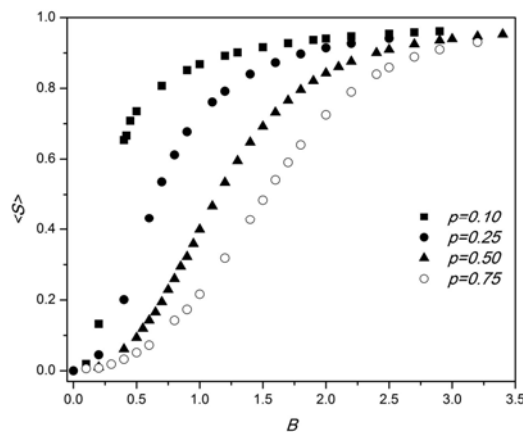


Fig.7 Memory effect RR, at a given T in the presence of external field B in different concentrations $p = 0.1, 0.25, 0.5$ and 0.75

IV. CONCLUSIONS

We used rod-like objects within a cubic lattice interacting via a Lebwohl–Lasher-type interaction. The structure of the system is described in terms of the director field S_i , where the unit vector S exhibits head-to-tile invariance. An example for this system represents LC molecules or nanotubes. In addition, we introduced impurities of concentration p , which impose the so-called random and homogenous anisotropy field. We analyzed the domain-type pattern of molecules as a function of p , anchoring strength w between a neighboring director and impurity.

Our results indicated that by increasing anchoring strength w , order parameter S decreased and by increasing impurities of concentration p and temperature correlation length ξ decreased too, because low impurities do not influence on neighbors so much, beside we have not seen significant difference between correlation function parameter (s) as a function of P in random and homogenous field.

Moreover, we analyzed memory effects for saturated configurations in the random initial configuration.

Our study reveals that when there is not external field $S=0$ it means SRO , but when we have external field it is $S > 0$.

ACKNOWLEDGMENT

Acknowledge from Slovenian Research Agency for training and financing of Young Researchers in Research Organizations.

REFERENCES

- [1] Zurek W.H. "Cosmological experiments in superfluid helium?" *Nature*, 1985, 317, 505.
- [2] Bray A.J. "Theory of phase-ordering kinetics" *Adv. Phys.* 1994, 43, 357.
- [3] Kibble T.W.B. "Topology of cosmic domains and strings" *J. Phys. A: Math. Gen.*, 1976, 9, 1387.
- [4] Imry Y.; Ma S. "Random-Field Instability of the Ordered State of Continuous Symmetry" *Phys. Rev. Lett.*, 1975, 35, 1399.
- [5] Feldman D.E. "Quasi-long-range order in nematics confined in random porous media" *Phys. Rev. Lett.*, 2000, 85, 4886.
- [6] Chakrabarti J. *Phys. Rev. Lett.* 1998, 81, 385.
- [7] Cleaver D.J.; Kralj S.; Sluckin T.J.; Allen M P. In *Liquid Crystals in "Complex Geometries Formed by Polymer and Porous Networks"* Crawford G.P. and Zumer S. Eds.; Oxford University Press: London, 1996.
- [8] Radzihovsky L. Toner "Anomalous Elasticity of Disordered Smectics" *J. Phys. Rev. Lett.*, 1997, 79, 4214.
- [9] Popa-Nita V. " " Statics and Kinetics at the Nematic-Isotropic Interface in Porous Media" " *Eur. Phys. J.*, 1999, 83, 12.
- [10] Popa-Nita V.; Romano S. " Nematic-Smectic A Phase Transition in Porous Media" *Chem. Phys.*, 2001, 91, 264.
- [11] De Gennes P.G.; Prost J. "The Physics of Liquid Crystals" Oxford University Press: Oxford, 1993.
- [12] Virga E.G. *Variational "Theories for Liquid Crystals"* Chapman Hall: London, 1994.
- [13] M.Ambrožič, S.Kralj, E.G.Virga "Defect-enhanced nematic surface order reconstruction" , *Phys. Rev. E*, 2007, 75, 031708 .
- [14] M.Ambrožič S. Kralj, T.J.Sluckin, S. Žumer, and D. Svenšek "Annihilation of edge dislocations in smectic-A liquid crystals" *Phys. Rev. E*, 2004, 70, 051704.
- [15] Lebwohl P.A.; Lasher G. "Nematic-Liquid-Crystal Order—A Monte Carlo Calculation", *Phys. Rev. A*, 1972, 6, 42.
- [16] M.Krasna, M.Cvetko, M. Ambrožič "Symmetry breaking and structure of a mixture of nematic liquid crystals and anisotropic nanoparticles", *Beilstein J. Org. Chem.* 6, No. 74, 2010.
- [17] Cruz, C.; Figueirinhas, J. L.; Filip, D.; Feio, G.; Ribeiro, A. C Frère, Y.; Meyer, T.; Mehl, G. H. "Biaxial nematic order and biaxial order and phase behavior studies in an organosiloxane tetrapode using complementary deuterium NMR experiments" *Phys. Rev. E*, 2008, 78, 051702.
- [18] Popa-Nita, V. "Statics and kinetics at the nematic-isotropic interface in porous media" *Eur. Phys. J. B*, 1999, 12, 83–90.
- [19] Popa-Nita, V.; Gerlič, I.; Kralj, S. Int. "The Influence of Disorder on Thermotropic Nematic Liquid Crystals Phase Behavior" *J. Mol. Sci.* , 10(9), 2009, 3971-4008.
- [20] Romano, S. Int. J. Mod. Phys. B " Computer simulation study of a Nematogenic Lattice-Gas model with fourth-rank interactions ", 2002, 16, 2901–2915.