FAR-FROM-EQUILIBRIUM DYNAMICS IN CALAMITIC AND BENT-CORE LIQUID CRYSTALS

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FAR-FROM-EQUILIBRIUM DYNAMICS IN CALAMITIC AND BENT-CORE LIQUID CRYSTALS

by

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School of Interdisciplinary Research (SIRe)

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To my parents, brother and late grandparents

Certificate

This is to certify that the thesis titled **"Far-From-Equilibrium Dynamics in Calamitic and Bent-Core Liquid Crystals"** *being submitted by* **Mr. Nishant Birdi** *to the Indian Institute of Technology Delhi for the award of the degree of* **Doctor of Philosophy** *in* **School of Interdisciplinary Research (SIRe)** *is a record of bonafide research work carried out by him under my supervision and guidance. He has fulfilled the requirements for the submission of the thesis, which to the best of my knowledge has reached the required standard.*

The material contained in this thesis has not been submitted in part or full to any other University or Institute for the award of any degree or diploma.

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Abstract

Liquid crystals (LCs) are an intermediate state of matter that amalgamate the fluidity of liquids with the long-range order of crystals. This is by virtue of the anisotropy in their structures. Due to this, they are the most preferred soft matter materials for optic and photonic applications. Also they have an equal contribution towards fundamental research as they provide a medium for observation of topological defects. These defects hold an interdisciplinary value as in them, the interest of researchers ranges over different disciplines. In this thesis, we study the equilibrium and non-equilibrium properties for LCs of two different shapes and huge technological importance: rod-shaped calamitics and banana-shaped bent-cores. We conduct extensive numerical investigations using discrete models which consider the interactions at molecular level. We select models which naturally incorporate the structural anisotropy in the molecules. Further the models are both experimentally relevant and computationally feasible.

An important non-equilibrium study we perform is of phase ordering dynamics where these LC systems are quenched to their desired LC phase(s). In each phase, the evolution of ordered domains occurs via annihilation of topological defects. Our primary aim is to characterize the evolution process and the topoligical defects observed during it. We provide the framework for it in terms of appropriate order parameters and various other quantifiers. For the calamitic LCs, we examine the nematic (Nm) phase which shows purely orientational order and the smectic (Sm) phase which displays an additional layering. The quenches made to both the phases are thermal. In the bent-core LCs, we explore the twist-bend (TB) nematic

phase which is a modulated nematic with helical order. In this case, we make a concentration quench.

To inspect the Nm phase, we utilize the lattice-based generalized Lebwohl-Lasher model which depending on the model parameter, is found to exhibit either a canted or an uniform arrangement between the nearest-neighbour LC molecules. We notice that the canted states show rough interfaces in 2-dimensional (2-d) systems and sharp interfaces in 3-d systems. On the other hand, uniform states are seen to exhibit disclination points in 2-d and strings of them in 3-d. Next we examine the Sm phase by employing the off-lattice Gay-Berne model. First the phase boundaries are located and then the quenches are performed. It is observed that the evolution of the Sm phase proceeds through a two-time-scale scenario in which first the Nm order evolves by annihilation of string defects. Later it is followed by layering where interfaces between these layers are the dominating defects. Finally for the bent-core LCs, we use curved spherocylinders interacting via the Weeks-Chandler-Andersen potential. Our findings reveal that a quench from the polar Sm phase to the chiral TB phase transpires through an intermediate splay-bend phase. This is a planar and S-shaped modulated phase. The dominating defects in the TB phase, termed as beta lines, are observed to be topologically analogous to the string defects found in the Nm phase. Other than these LC phases, this set of novel results emerging from the current work will be relevant for a large class of systems with multiple kinds of orientational orderings. We anticipate that this work triggers-off stimulating (experimental) investigations in them.

In the end, we provide conclusions and various future perspectives, ideas, developments, etc originating from the work discussed in this thesis.

सार

द्रव क्रिस्टल (एलसी) पदार्थ की एक मध्यवर्ती अवस्था है जो द्रवों की तरलता को क्रिस्टलों की दीर्घ–सीमा क्रम के साथ मिश्रित कर देती है। ऐसा उनकी संरचनाओं में विषमता के कारण होता है। इस कारण, वे प्रकाशिक और फोटोनिक अनुप्रयोगों के लिए सबसे पसंदीदा नरम पदार्थ सामग्री हैं। साथ ही, मौलिक अनुसंधान में भी उनका समान योगदान है क्योंकि वे स्थलाकृतिक दोषों के अवलोकन के लिए एक माध्यम प्रदान करते हैं। इन दोषों का एक अंतःविषयक मूल्य है क्योंकि इनमें शोधकर्ताओं की रुचि विभिन्न विषयों में होती है। इस शोध प्रबंध में, हम दो अलग–अलग आकृतियों और विशाल तकनीकी महत्व वाले एलसी के संतुलन और गैर–संतुलन गुणों का अध्ययन करते हैं: छड़ के आकार के कैलामाइटिक्स और केले के आकार के बेंट–कोर। हम असतत मॉडलों का उपयोग करके व्यापक संख्यात्मक जांच करते हैं जो आणविक स्तर पर अंतःक्रियाओं पर विचार करते हैं। हम ऐसे मॉडलों का चयन करते हैं जो स्वाभाविक रूप से अणुओं में संरचनात्मक विषमता को शामिल करते हैं। इसके अलावा ये मॉडल प्रयोगात्मक रूप से प्रासंगिक और कम्प्यूटेशनल रूप से व्यवहार्य दोनों हैं।

एक महत्वपूर्ण गैर–संतुलन अध्ययन जो हम करते हैं वह चरण क्रम गतिकी का है जहाँ इन एलसी प्रणालियों को उनके वांछित एलसी चरण(चरणों) तक बुझाया जाता है। प्रत्येक चरण में, क्रमबद्ध डोमेन का विकास टोपोलॉजिकल दोषों के विनाश के माध्यम से होता है। हमारा प्राथमिक उद्देश्य विकास प्रक्रिया और उसके दौरान देखे गए राजनीतिक दोषों को चिह्नित करना है। हम इसके लिए उपयुक्त क्रम पैरामीटर और विभिन्न अन्य परिमाणकों के संदर्भ में रूपरेखा प्रदान करते हैं। आपदाजनक एलसी के लिए, हम नेमैटिक (एनएम) चरण की जाँच करते हैं जो विशुद्ध रूप से अभिविन्यासीय क्रम दर्शाता है और स्मेक्टिक (एसएम) चरण की जाँच करते हैं जो एक अतिरिक्त परत प्रदर्शित करता है। दोनों चरणों में किए गए शमन तापीय हैं। बेंट–कोर में, हम ट्विस्ट–बेंड (टीबी) नेमैटिक चरण का अन्वेषण करते हैं, जो कुंडलित क्रम वाला एक मॉड्युलेटेड नेमैटिक है। इस स्थिति में, हम एक सांद्रण शमन करते हैं।

एनएम चरण का निरीक्षण करने के लिए, हम जाली–आधारित सामान्यीकृत लेबवोहल–लाशर मॉडल का उपयोग करते हैं, जो मॉडल पैरामीटर के आधार पर, निकटतम पड़ोसी एलसी अणुओं के बीच या तो एक तिरछी या एक समान व्यवस्था प्रदर्शित करता है। हमने देखा कि कैंटेड अवस्थाएं 2–आयामी (2–डी) प्रणालियों में खुरदुरे इंटरफेस और 3–डी प्रणालियों में तीक्ष्ण इंटरफेस दिखाती हैं। दूसरी ओर, एकसमान अवस्थाएँ द्वितीय–दिव्य में विभेदन बिंदु और तृतीय–दिव्य में उनकी श्रृंखलाएँ प्रदर्शित करती देखी जाती हैं। इसके बाद, हम ऑफ–लैटिस गे–बर्न मॉडल का उपयोग करके एसएम चरण की जाँच करते हैं। सबसे पहले प्रावस्था सीमाएँ निर्धारित की जाती हैं और फिर शमन किया जाता है। यह देखा गया है कि एसएम प्रावस्था का विकास एक द्वि–समय–पैमाने परिदृश्य से होकर गुजरता है जिसमें सबसे पहले स्ट्रिंग दोषों के विनाश द्वारा एनएम क्रम विकसित होता है। इसके बाद परतों का निर्माण होता है जहाँ इन परतों के बीच के अंतरापृष्ठ प्रमुख दोष होते हैं। अंत में बेंट–कोर के लिए, हम वीक्स–चांडलर–एंडरसन विभव के माध्यम से परस्पर क्रिया करने वाले घुमावदार स्फेरोसिलिंडर का उपयोग करते हैं। हमारे निष्कर्षों से पता चलता है कि ध्रुवीय एसएम चरण से किरल टीबी चरण तक शमन एक मध्यवर्ती स्प्ले–बेंड चरण के माध्यम से होता है। यह एक समतलीय और एस–आकार का मॉड्युलेटेड चरण है। टीबी चरण में प्रमुख दोष, जिन्हें बीटा रेखाएँ कहा जाता है, टोपोलॉजिकल रूप से एनएम चरण में पाए जाने वाले स्ट्रिंग दोषों के समान पाए जाते हैं। इन एलसी चरणों के अलावा, वर्तमान कार्य से उभरने वाले नए परिणामों का यह समूह कई प्रकार के अभिविन्यास क्रमों वाले प्रणालियों के एक बड़े वर्ग के लिए प्रासंगिक होगा। हमारा अनुमान है कि यह कार्य उनमें उत्तेजक (प्रयोगात्मक) जाँच–पड़ताल को गति प्रदान करेगा।

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List of abbreviations

BCLC	Bent-core liquid crystal
GB	Gay-Berne
GLL	Generalized Lebwohl-Lasher
GS	Ground states
LAC	Lifshitz-Allen-Cahn
LC	Liquid crystal
LJ	Lennard-Jones
LL	Lebwohl-Lasher
MC	Monte Carlo
MCS	Monte Carlo step
MD	Molecular dynamics
Nm	Nematic
nn	nearest neighbour
PBC	Periodic boundary condition
SB	Splay-bend
Sm	Smectic
SU	Super-universality
TB	Twist-bend
WCA	Weeks-Chandler-Andersen