

STUDY OF INTERFACIAL PROPERTIES IN LIQUID CRYSTALS USING MOLECULAR DYNAMICS SIMULATIONS

A THESIS

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by

Jagroop Kaur

(Regn. No. 901612005)

Under the supervision of

Dr. Debabrata Deb

Associate Professor



DEPARTMENT OF PHYSICS AND MATERIAL SCIENCE
THAPAR INSTITUTE OF ENGINEERING AND TECHNOLOGY,
PATIALA, PUNJAB-147004, INDIA

JUNE 2026

Dedicated to
My family

CERTIFICATE

This is to certify that the thesis entitled “**STUDY OF INTERFACIAL PROPERTIES IN LIQUID CRYSTALS USING MOLECULAR DYNAMICS SIMULATIONS**” being submitted by **Ms. Jagroop Kaur** for the fulfillment of the requirements for the award of the Doctor of Philosophy degree in the Department of Physics and Material Science, Thapar Institute of Engineering and Technology, Patiala, is a record of the candidate's own work carried out by her under my supervision. The matter presented in this thesis has not been submitted in part or full for the award of any degree in any other university or institute.

Supervisor



Dr. Debabrata Deb

Associate Professor

DPMS

TIET, Patiala- 147004

Punjab (India)

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Patiala

Jagroop Kaur

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Contents

Abstract	1
Outline of the thesis	3
1 Introduction	5
1.1 Nucleation in materials composed of isotropic particles	7
1.2 Liquid crystalline droplets	11
1.3 Crystallization in LCs	13
1.4 Isotropic-Nematic interface	15
1.5 Fluctuating interface	17
1.6 Isotropic-Smectic interface	19
1.7 Nematic-Smectic B interface	20
1.8 Wetting phenomenon in LCs	22
1.9 Surface anchoring during wetting	24
1.10 Complete or incomplete wetting	25
1.11 Motivation of the thesis	26
2 Theoretical formalism	29
2.1 Homogeneous and heterogeneous nucleation	29
2.2 Molecular dynamics simulations technique	34
2.2.1 Microcanonical ensemble (NVE)	37
2.2.2 Canonical ensemble (NpT and NVT)	38
2.3 LAMMPS	42
2.3.1 Initialization	43
2.3.2 Simulation settings	45
2.3.3 Running the simulations	45
2.3.4 Data collection	46
2.4 Liquid crystals	47
2.5 Interaction potential models	48
2.5.1 Gay-Berne potential model	48
2.5.2 Weeks-Chandler-Anderson potential	51
2.6 Computation of the interfacial properties	52
2.6.1 Capillary wave theory (CWT)	52

2.6.2	Pressure tensor (PT) method	53
3	Interfacial stiffness of Gay-Berne nematic-smectic B interface	63
3.1	Introduction	63
3.1.1	Simulation details	65
3.2	Results and discussion	66
3.2.1	Phase recognition	66
3.2.2	Coexistence density range	70
3.2.3	nm-smB interfacial energy	74
3.3	Summary and conclusion	74
4	Interfacial tension between Gay-Berne isotropic fluid and wall	77
4.1	Introduction	77
4.1.1	Simulation details	78
4.2	Results and discussion	80
4.2.1	MD simulation snapshots, pressure tensor profiles and nematic order parameter.	80
4.2.2	Density and local orientational order profiles	85
4.2.3	Interfacial tension	88
4.3	Summary and conclusion	93
5	Droplet morphology in the nematic-smectic B phase coexistence	97
5.1	Introduction	97
5.2	Simulation details	99
5.3	Results and discussion	101
5.3.1	Phase identification with a sub-box technique	102
5.3.2	Shapes of nm and smB droplets	106
5.4	Summary and conclusion	113
6	Summary and concluding remarks	115

List of Tables

3.1	The coexistence density range for nm and smB phases for different system sizes using density profiles	73
4.1	Data for smaller system size with GB ellipsoids confined between two WCA walls obtained from MD-NVT simulations	90
4.2	The literature values of interfacial and surface tension for various model systems	92
5.1	Time taken by simulations with different CPU cores and system sizes	101

List of Figures

1.1	The plot of chemical potential versus density describes the morphology of droplets (liquid or vapor) formed in the case of Lennard-Jones fluid	8
1.2	Different phases of thermotropic liquid crystals	11
1.3	A nematic GB droplet coexisting with its vapor phase	12
1.4	A crystalline cluster in a metastable isotropic liquid was obtained in a fluid of hard spherocylinders	14
1.5	The isotropic-nematic interface in the case of GB liquid crystalline system	17
1.6	A sketch of the interfacial fluctuations or the capillary waves	18
1.7	The isotropic-smectic interface in the case of GB liquid crystalline system	19
1.8	Different shapes of smectic-B germs in nematic phase in a quasi-two-dimensional geometry	21
1.9	Wetting of the crystalline surface by equilibrated nematic nanodroplets from the vapor phase was observed upon increasing affinity	23
1.10	A pictorial representation of liquid crystalline particles on the surface with parallel, homeotropic, and oblique anchoring	24
1.11	The pictorial illustration of the wetting behavior of droplets on the surface with bad, good, and complete wetting	26
2.1	A cartoon image showing the homogeneous nucleation and the variation of free energy with the cluster size is shown	30
2.2	A cartoon image illustrating the heterogeneous nucleation phenomenon and the Young's equation	32
2.3	A sketch of the free energy barriers associated with the homogeneous and heterogeneous nucleation	33
2.4	The Gay-Berne interaction potential and phase diagram	50
2.5	The soft, smooth, and repulsive Weeks-Chandler-Anderson (WCA) interaction potential between the wall and particle.	51

2.6	A reference image of a cuboidal box containing GB ellipsoids confined by two WCA walls	54
3.1	The snapshots showing the coexistence of nematic (blue) and smectic-B (pink) phases and only the smectic-B phase	67
3.2	The relative angle between the nematic and smectic directors of the system with the nm-smB interface for various system sizes	69
3.3	The variation of the nematic phase width of the system with time	70
3.4	Density profiles in the nematic-smectic B coexisting system	71
3.5	Mean squared interfacial width versus natural logarithm of lateral size of box	73
4.1	The snapshots (yz -view) of system size, $L = 27.9841$ and $L_z = 58.2131$, are shown with wall at various number densities	81
4.2	The reduced pressure tensor profiles for $L = 27.9841$ and $L_z = 58.2131$ for various number densities	82
4.3	The variation in the nematic order parameter calculated near the wall upon increasing bulk number density	83
4.4	The snapshots (yz -view) of system size, $L = 29.4111$ and $L_z = 91.8788$, are shown with wall at various number densities	84
4.5	The reduced pressure tensor profiles for $L = 29.4111$ and $L_z = 91.8788$ for various number densities	84
4.6	The number density and local orientational order profiles for two overall densities are exhibiting the homeotropic alignment of particles near the wall	86
4.7	The local orientational order profiles $Q_{zz}(z)$ for system size are shown for various number densities with bulk isotropic phase	87
4.8	The variation of reduced interfacial tension with bulk number densities is shown with error bars for two system sizes	89
4.9	The reduced wall-isotropic interfacial tension versus bulk number density for four WCA wall strengths	90
5.1	The plots of the orientational order distributions at different number densities for smaller system size	103
5.2	The plots of the orientational order distributions at different number densities for larger system size	104
5.3	The plots of number density distributions at different number densities for larger system size	105
5.4	The snapshots exhibiting the whole system and the droplet without the interface at different viewing angles at lower nm-smB coexisting number densities for smaller system size	107
5.5	A cartoon picture shows different scenarios of a microscopic droplet formed in a subdivided simulation box	108

5.6	The snapshots exhibiting the whole system and droplet without the interface at different viewing angles at higher nm-smB coexisting number densities for smaller system size.	110
5.7	The snapshots exhibiting the whole system and droplet without the interface at different viewing angles at lower nm-smB coexisting number densities for larger system size	111
5.8	The snapshots exhibiting the whole system and droplet without the interface at different viewing angles at higher nm-smB coexisting number densities for larger system size	112
5.9	One-dimensional morphology diagram along the nm-smB phase co-existence line for GB LC material	114

List of Publications

I. International Journals:

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Abstract

In this thesis, the nucleation phenomenon in a thermotropic liquid crystalline system is investigated using the molecular dynamics simulations technique. The interaction between liquid crystalline (LC) particles is modeled by using the Gay-Berne (GB) potential model. To understand the nucleation or interfacial phenomenon in GB LCs, the interfacial stiffness of the nematic-smecticB (nm-smB) interface in an unconfined and the interfacial tension of the wall-isotropic fluid (wall-iso) interface in a confined GB LC system are calculated.

For the unconfined GB system, we have mainly focused on analyzing the interfacial phenomenon with nematic (nm) and smectic-B (smB) phases due to inadequate studies on the nm-smB interface in the literature. The interfacial stiffness of the nm-smB interface is calculated using capillary wave theory. The identification of nm and smB phases separated by a planar interface is done by using a particle-based local bond order parameter. In addition, the morphology of homogeneous nm and smB droplets formed within the nm-smB coexistence is also analyzed. To identify the coexisting nm and smB phases separated by planar and non-planar interfaces, we have developed a local-averaging technique based on the orientational order parameter. This identification criterion helped us to determine the aspherical, cylindrical, and planar shapes of nm and smB droplets formed in the system.

In a confined system, the GB isotropic fluid is confined by soft, smooth, and repulsive walls. The interaction between GB particles and walls is defined by the Weeks-Chandler-Anderson (WCA) potential model. The interfacial tension of the interface between GB isotropic fluid and WCA wall (wall-iso interface) is determined using the pressure tensor method. The effect of the wall-particle interaction strength on the wall-iso interfacial tension is analyzed. Moreover, the finite-size effects on the interfacial phenomenon in confined and unconfined systems are also studied.

Thesis layout

This thesis consists of six chapters, which are arranged in the following way:

- **Chapter 1** begins with a general introduction and review of the literature related to our work. It includes the work already done to understand the homogeneous nucleation and wetting phenomenon in materials containing spherical particles. The interfacial studies in the liquid crystalline material for different interfaces, such as isotropic-nematic, isotropic-smectic, and nematic-smectic interfaces, are reviewed. At the end of this chapter, the motivation and objectives of this thesis are mentioned.
- **Chapter 2** details our work's methodology and theoretical formalism. The homogeneous and heterogeneous nucleation phenomena are briefly described, and free energy is defined for both nucleation processes. Detailed information about the MD simulation technique and the LAMMPS package is given. Different types, applications, and phases of LCs are depicted. The models used to define the LC particle-particle interaction (i.e., Gay-Berne (GB) potential) and the LC particle-wall interaction (i.e., Weeks-Chandler-Anderson (WCA) potential) are described in detail. In this work, we have determined the interfacial stiffness in an unconfined and interfacial tension in a confined GB LC system. The theoretical methods, such as capillary wave theory (CWT) and pressure tensor (PT) method, used to compute the interfacial properties are briefly described in this chapter.
- In **Chapter 3**, the nematic-smectic B (nm-smB) phase coexistence is observed in GB (3, 5, 2, 1) system using MD simulations. By analyzing the density profiles along a direction transverse to the interface, the nm-smB phase coexisting

density range is calculated. Then, using the local bond order parameter q_6q_6 , the particles belonging to the nematic and smectic-B phases are distinguished. Therefore, we have been able to directly observe the existence of a rough and fluctuating interface separating the two phases. These observations led us to use CWT to determine the interfacial stiffness of the nm-smB interface.

- In **Chapter 4**, the MD simulation results of GB isotropic fluid confined by two WCA walls for a wide range of number densities are shown. The aperiodic confinement due to walls makes the system mechanically anisotropic. Hence, using the PT method, the interfacial tension of an interface between the bulk isotropic (I) phase and WCA wall at various number densities (ρ) is calculated. In addition, the effects of the system size and wall-GB interaction strength on the wall-isotropic interfacial tension are also presented.
- In **Chapter 5**, different morphologies of the homogeneous nematic (nm) and smectic-B (smB) droplets formed within the nm-smB phase coexistence are observed in the unconfined GB system at various number densities (ρ). To identify the nm and smB phases, we have developed a local-averaging method in which the orientational order parameter (S_{sb}) is calculated in small sub-boxes of the simulation box. Hence, using the S_{sb} distributions, we have an identification criterion to identify the nm and smB phases. Using such a local-averaging technique, the aspherical, cylindrical, and planar shapes of nm and smB droplets are observed within the nm-smB coexistence. The effect of finite-system size on the morphology of these droplets is also shown.
- At the end, in **Chapter 6**, the results drawn from our study, as discussed in the above chapters, are summarised. Additionally, the future scope of our present work is briefly discussed.

Chapter 1

Introduction

There are various fascinating phenomena, whether natural or artificial, that take place around us. It has always been the human quest to reason the occurrence of these events. For instance, cloud and foam formation, brisk formation of bubbles in carbonated water upon adding a rough-surfaced candy, the impure water freezes at around 5°C , and pure water freezes at a temperature less than -35°C , water in a bottle remains liquid even if it is cooled down to -18°C but it instantly freezes into ice as the bottle is shaken, and so on. All these phenomena are governed by a thermal and heterogeneity-activated process known as the nucleation [1,2,3,4]. The nucleation phenomenon includes the generation of a new thermodynamically stable phase from a metastable mother phase through self-assembly or self-organization. The mother and new phases coexist during nucleation and are separated by an interface. Therefore, nucleation is also known as the interfacial phenomenon. Nucleation can be observed in various industrial, technological, biological, natural, and household activities [5,6]. Thorough knowledge of the nucleation phenomenon is crucial in various areas of science and technology, such as atmospheric science, material science, cosmochemistry, aerosol formation, etc. Nucleation is broadly categorized into two types, namely homogeneous and heterogeneous nucleation. The spontaneous emergence of a droplet of new phase from a moderately supersaturated mother phase via statistical fluctuations is known as the homogeneous nucleation [1]. On

the other hand, heterogeneous nucleation occurs in the presence of an impurity, such as walls of a container, dust particles, etc., which promotes nucleation and hence reduces the nucleation barrier [1]. The original theory to understand homogeneous nucleation is the classical nucleation theory (CNT) [1, 7, 8, 9, 10, 11]. According to CNT, the small nuclei of the new phase formed due to thermal fluctuations disappear or grow if the fluctuations are small or large, respectively. As these nuclei grow, they become stable only if they achieve a critical size; otherwise, they might shrink and dissolve in the mother phase. The emergence rate of these critical nuclei is known as the nucleation rate, which determines the time required for a phase transition or nucleation to occur. Beyond the critical size, the nucleus generally grows faster than the rate with which it forms. The basic assumptions in CNT are straightforward but invalid under many circumstances (discussed briefly in chapter 2). Therefore, CNT has several limitations [3, 4, 12], and many new approaches have been developed for the critical understanding of the nucleation phenomenon [13]. The phase transitions occurring via nucleation are of the first-order and, thus, must cross a kinetic barrier. The observations that indicate the presence of kinetic barrier are the cooling of highly purified tiny water droplets in capillary tubes below -30°C without freezing, the undercooling of emulsified gallium droplets at around 150°C below their freezing point (30°C), the compression of gas for pressure higher than its condensation pressure, and so on.

Nucleation is a slow process because a metastable phase persists for a very long time [13]; thus, an observer has to wait for an eventuality to observe a nucleation event. Therefore, such rare events are tedious to study using conventional simulation techniques because they involve a lot of CPU time. Consequently, elementary models, such as Ising model, and a very large supersaturation having a few $k_B T$ of nucleation barrier [2, 14, 15, 16, 17], have been used to study the nucleation kinetics using simulations. The simulation techniques, such as transition-path-sampling, umbrella-sampling, or forward-flux-sampling methods [18], Monte Carlo (MC) [19, 20] and

SECTION 1.1: NUCLEATION IN MATERIALS COMPOSED OF ISOTROPIC PARTICLES

Molecular Dynamics (MD) [11, 21, 22, 23] have been used to investigate the nucleation phenomenon. The MD technique helps to observe the nucleation event directly and thus has been widely used to investigate the nucleation phenomenon in different model systems [24]. These simulation studies reported various nucleation pathways with metastable states that minimize the loss of free energy during the nucleation, thus enhancing our understanding of the mechanism.

1.1 Nucleation in materials composed of isotropic particles

The nucleation phenomenon in the case of spherical particles is widely studied using computer simulations [25] and theoretical approaches [13, 18, 26]. These studies found that the structure at the core of the central nucleus might vary entirely from the new bulk phase formed. Also, the interface between the critical nucleus and the metastable state may be represented by a density and structural profile that is not sharp and step-like [13, 18, 25, 26]. There are various theoretical, experimental and simulation studies which have investigated the mechanism of homogeneous nucleation [1, 14, 21, 27, 28, 29]. Generally, homogeneous nucleation or droplet formation involves three stages of phase transformation. The first stage is droplet nucleation, followed by the second stage of droplet growth because of the lower free energy of larger droplets. The growth speed depends on the degree of undercooling or the difference in free energy between the two phases. The third stage involves the coalescence of larger droplets. The condensation process (i.e., gas-to-liquid transition) occurs with the formation and expansion of molecular clusters. It has been well studied using Volmer's classical theory, Mayer's theory of condensation, etc. [30]. During the vapor-liquid coexistence in Lennard-Jones (LJ) fluid, different shapes of vapor (or liquid) droplets have been observed in the mother liquid (or vapor) phase, respectively [14, 31]. Schrader *et al.* [14] plotted chemical potential (μ) versus den-

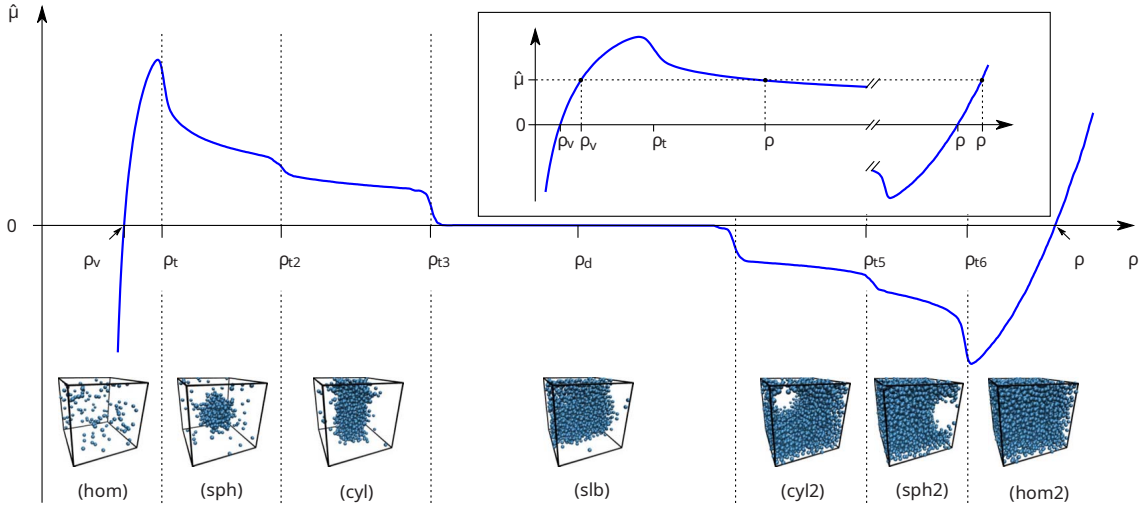


Figure 1.1: The plot of chemical potential versus density describes the morphology of droplets (liquid or vapor) formed in the case of Lennard-Jones fluid in a finite cubical box as reported by Schrader *et al.*, *Phys. Rev. E* **79**, p. 061104 (2009) [14]. The image is taken from [14]

sity (ρ) (as shown in Fig. 1.1) to understand the morphology of droplets formed. From the plot (Fig. 1.1), it was seen that in a finite cubical box, $\mu = 0$ at $\rho = \rho_l$ or $\rho = \rho_v$ corresponded to the homogeneous liquid or vapor phase, respectively, which can coexist with each other in the thermodynamic limit. The homogeneous vapor or liquid can exist at $\rho > \rho_v$ or $\rho < \rho_l$, with $\mu \neq 0$, till the state of condensation or evaporation, respectively. As the system density exceeded the condensation density, a spherical liquid droplet coexisted with the supersaturated vapor. A further increase in density led to a cylindrical droplet sustained within the vapor. However, in the central region with $\rho = (\rho_l + \rho_v)/2$, the liquid and vapor coexisted in a slab configuration. Upon a further increase in density, a cylindrical and then spherical-shaped bubble coexisted with liquid. At further higher densities, the stable homogeneous liquid phase was observed.

Furthermore, the solid-liquid nucleation has also been well investigated in various studies [32]. In the crystallization process, a critical-sized crystallite nucleates from the liquid, and then grows to macroscopic dimensions. As the crystal grows rapidly, only the nucleation rate, in the first step, controls the freezing rate of an

SECTION 1.1: NUCLEATION IN MATERIALS COMPOSED OF ISOTROPIC PARTICLES

undercooled liquid. During the rapid crystal growth, the critical nucleus can not be directly studied. Therefore, it is difficult to experimentally measure the minimum temperature required to supercool the tiny liquid droplets before crystallizing. As a result, various experiments [32] have been conducted in the original extensive temperature measurements by Turnbull [29] for various liquid metals. During the isotropic (liquid)-crystal coexistence, the thermal energy of the isotropic liquid is higher than that of a crystalline solid. Therefore, a crystal would have to gain some energy to convert it into a liquid, and a liquid would have to lose some energy to become a crystal. This results in a nucleation barrier that needs to be overcome for the nucleating crystals to grow. The thickness of an interface formed between isotropic liquid and crystal phases tells the strength of the interfacial tension. If this thickness is small, the interfacial tension would be large and vice-versa. At the coexistence pressure, P_{co} , no thermodynamic force drives the system away from coexistence. As a result, the system's average volume does not fluctuate with time. However, when a thermodynamic parameter like ρ or T is changed, crystallization may occur, and the kinetics of such a process has been well studied by several authors in the case of spherical colloidal particles [33, 34].

Moreover, a nucleation site, such as an impurity or surface, triggers various fascinating surface phenomena such as adsorption, wetting, etc. Therefore, wetting (or heterogeneous nucleation) occurs much more often and thus can be easily observed. Several technologies, namely gluing, coating, dyeing, etc., are based on the wetting of the solid surface by fluid droplets. During the surface wetting by a fluid, the surface may allow the fluid to spread over it entirely, or sometimes more ordered phases may develop. In materials composed of isotropic particles, the heterogeneous nucleation has been well studied using various model systems [4], resulted in spherical cap-shaped droplets [35]. Therefore, considerable empirical knowledge of the nucleation phenomenon has been gained in a system of isotropic particles. However, in nature, there are molecular materials made up of aspherical particles, such as

liquid crystalline material. The shape anisotropy of particles in liquid crystalline material makes the phase diagram rich [36, 37, 38, 39, 40, 41]. Therefore, studying interfacial properties reveals the interesting interfacial phenomenon in liquid crystals. In this thesis, we have presented the study of the interfacial phenomenon in thermotropic calamitic liquid crystals (LCs) [42, 43]. The thermotropic LCs exhibit several phases upon changing the temperature, such as isotropic, nematic, smectics, crystalline, etc. (Fig. 1.2) [42, 44]. The isotropic phase does not have any positional and orientational order. The nematic phase does not have long-range positional order but has a long-range orientational correlation, in which a vector, called director $\mathbf{n}$, defines the average orientation of molecules (Fig. 1.2). In the smectic phase, the molecules orienting in the same direction are also arranged in layers resulting in both the positional and orientational order. Further, depending upon the angle between the director ($\mathbf{n}$) and layer normal, the smectic phase is of different types, such as smectic-A, smectic-B, and smectic-C. In the smectic-A (smA) and smectic-C (smC) phases, there is no positional order within the layers, but the director is along the layer normal in the smA phase and tilted to the layer normal in the smC phase. The smectic B (smB) phase has a director along the layer normal like the smA phase, but has a hexagonal crystalline order in each layer, which are not correlated. However upon decreasing temperature, if these layers are locked like a (1, 1, 1) plane in fcc or hcp lattice, then a crystalline phase is formed (Fig. 1.2). Such a rich phase behavior of LCs has helped them to find their use in technologically diverse applications [45, 46, 47, 48, 49, 50, 51] like LC displays, electrically controlled phase shifters, polarization rotators, optical switches, etc. To prepare suitable LC materials for their diverse applications, precise material processing methodologies are required, which would be developed with a better understanding of the nucleation and growth phenomena.

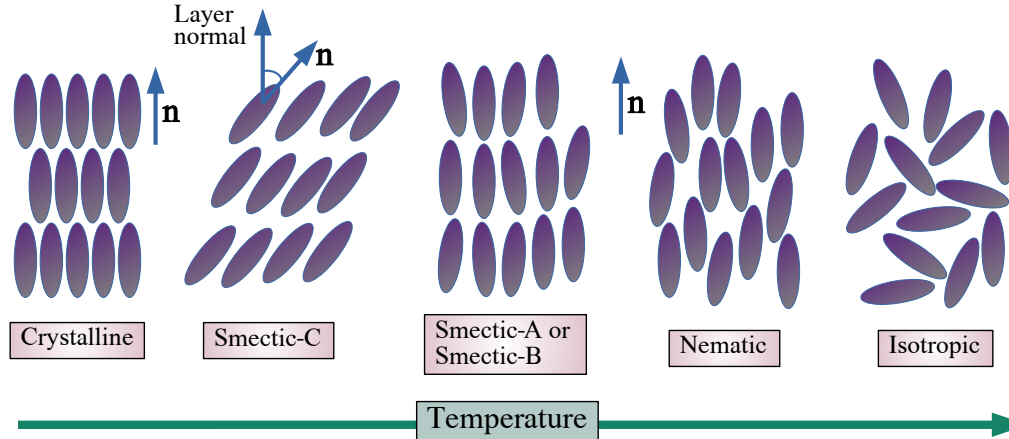


Figure 1.2: Different phases of thermotropic liquid crystals are shown, with the isotropic phase having no order and the nematic phase having only the orientational order. The smectic-A (smA) and smectic-C (smC) phases have particles arranged in layers with no positional order within the layers. However, in the smA and smC phases, the director ($\mathbf{n}$) is along and tilted to the layer normal, respectively. The smectic-B (smB) phase is like the smA phase but has a hexagonal crystalline order in each layer, which are not correlated. However, if these layers are locked like a (1, 1, 1) plane in an fcc or hcp lattice, then a crystalline phase is formed (adapted from the work done by Ian Cadenhead, Thesis, University of Colorado Boulder (2019) [52])

1.2 Liquid crystalline droplets

In contrast to nucleation in materials with isotropic particles, the nucleation in nematic LCs is complicated due to the free energy cost when the droplets coalesce because the directors point in different directions in adjacent droplets. The majority of studies on anisotropic particles examined the nematic droplets as micro-domains in isotropic fluid [53] because they exhibit an interesting interfacial phenomenon. The nucleation of the nematic phase can occur via a phase-ordering kinetic process [54] by quickly developing the local order and gradually expelling the topological defects in the system. These nematic droplets are generally small, and the free energy required to stabilize an interface is very large. As a result, the nematic droplets are not energetically favored and get easily dissolved. However, the decrease in the surface energy cost of the droplet thermodynamically favors the nucleation of a sufficiently large droplet [54]. In contrast, the small-sized droplets in the suspensions do not remain stable for a long time, and they aggregate into a single large droplet

[55]. During the melting of free-standing smectic films [56, 57], the isotropic or nematic droplets grew due to material release from the growing dislocation loops and further coalesced to form larger droplets. The attraction between the droplets occurred via the capillary forces arising due to surface energy gradients between the droplets [56]. Various studies show that the shape of LC droplets can deviate from

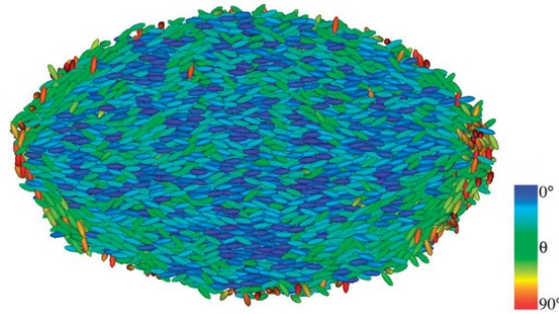


Figure 1.3: A nematic GB droplet in coexistence with the vapor phase. The color coding indicates the orientation of GB particles with respect to the droplet's principal inertia axis (θ). The image is taken from the work done by Vanzo *et al.*, *Soft Matter* **8**, p. 11790-11800 (2012) [58]

circular or spherical [59] (Fig. 1.3). This is because the interfacial energy at the surface of the nematic droplet competes with the particles' ability to orient along a single director in the nematic phase. Such a competition between volume (or bulk) and surface (or interfacial) energies may lead to non-spherical droplets, which are often observed in the case of small-sized droplets [24]. Therefore, in contrast to other fluid systems, bulk properties overpower the interfacial effects in the case of smaller liquid crystalline droplets [24]. For instance, the study of nematic droplets in smectic membranes found large circular nematic droplets and small elongated droplets at low temperatures [59]. However, the spindle-like droplets were found with two cusps on their boundary at high temperatures due to the competing elastic and interfacial energies. Various experimental [60, 61, 62, 63] and simulation [18, 64] studies on the assembly of nematic phase have resulted into the elongated spindle-shaped nematic droplets known as tactoids [61]. These tactoids can grow via Ostwald ripening [65] or coalescence [60, 66] to form Schlieren patterns [67]. Further, regarding the droplet

growth, some studies observed the droplet elongation along the particles' director [55, 58, 67, 68, 69] whereas others found the elongation direction different than of the director [70]. The smectic or crystalline droplets in LCS have also been well investigated using experiments [71, 72] and simulations [73, 74], but simple transient droplets were not observed. The crystal formation and growth in LCS are discussed in the next section.

1.3 Crystallization in LCS

In contrast to spherical systems, the crystal nucleation pathways are more complicated in systems containing anisotropic particles [75]. The crystallization in the case of spherical particles results in roughly spherical crystal nuclei [73]. On the other hand, the aspherical molecules crystallize by forming strongly anisometric crystals. It might be due to different interfacial free-energy densities for different crystalline faces, i.e., parallel and perpendicular to the molecular axes, leading to the aspherical equilibrium shape of small crystal nuclei. Beyond the critical size of the crystal nuclei, the rate of further molecular incorporation into the crystal may be strongly dependent on the nature of the crystalline face. This may result in the development of extremely long liquid crystal fibers [73]. Sometimes, the presence of an impurity can inhibit the growth of one or more crystal facets as it can be strongly adsorbed onto the growth front and thus poisons the further addition of molecules into that facet. These impurities might not be the chemical ones but the misaligned or misfolded representations of the crystallizing species [73]. Therefore, the crystal growth is hampered due to these defects present in the crystal, which is known as self-poisoning. For instance, in the case of long rods, the slow dynamics inhibited the nucleation of the smectic phase [74]. In an isotropic-to-crystal nucleation study of a colloidal suspension of short hard spherocylinders (Fig. 1.4), self-poisoning occurred because the crystal nucleus, being free of defects, was surrounded by a liquid layer of molecules aligned differently than the crystallite director [73]. As a result,

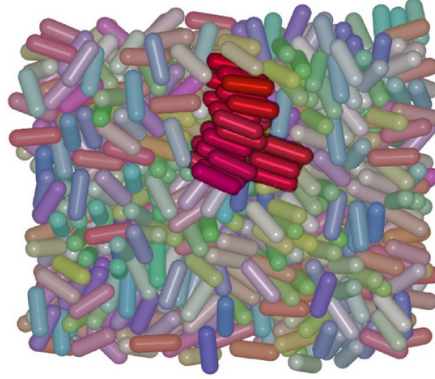


Figure 1.4: A crystalline cluster (red colored) in a metastable isotropic liquid was obtained in a fluid of hard spherocylinders. The image is taken from Schilling *et al. Phys. Rev. Lett.* **92**, p. 085505 (2004) [73], where the color coding indicates the particles' orientations

the second-layer crystal growth was difficult because the particles needed to be pre-aligned to be added into the crystals, which cost free energy. Then, a nucleation event was required to form a compact cluster that could be further expanded to a larger size. In the above study, the cluster size-dependent free energy was calculated, which showed that the system never reached the nucleation barrier for the spontaneous growth of crystallites [73,75]. As a result, at sufficiently high supersaturation, the multilayer crystal growth was kinetically suppressed. In contrast, the lateral growth remained unhampered, which ultimately resulted in disk-like [72] or raft-like [76] crystallites [73]. The multilayer growth of the crystals can be facilitated by using an orientationally biased field, such as a strong and static magnetic field [73]. In the case of aspherical particles, when the compression of the disordered phase, even at very high densities, does not result in spontaneous crystallization, then the structure and free energy of small crystal nuclei can be determined by using the biased sampling techniques [75].

In further sections, we have discussed the interfaces formed in an LC system, such as isotropic-nematic, isotropic-smectic, and nematic-smectic interfaces. The simplest fluid-fluid interface, apart from the liquid-vapor surface, is the isotropic-nematic (iso-nm) interface. In the experimental studies of the iso-nm interface,

pressure is not considered an important parameter because both phases are incompressible. Moreover, the isotropic and nematic phases have small density differences, so density is believed not to influence the interfacial properties [77].

1.4 Isotropic-Nematic interface

The iso-nm interface has been widely studied using theoretical [54, 77, 78, 79, 80, 81, 82, 83], experimental [84, 85], and simulation methods [86, 87, 88, 89, 90, 91, 92]. During iso-nm coexistence, the translational and orientational symmetry are broken at the interface, and thus the interfacial profiles can be analyzed by using the density and orientational order profiles [77, 78, 86, 93]. Measuring the interfacial width by fitting the hyperbolic tangent function to the simulated density profile has led to a good description of the iso-nm [93] interface. The iso-nm interfacial properties have been computed using various techniques in different model systems, such as using spherical harmonic expansion in rod-like system [78, 81], pendant drop technique for semiflexible polymer [94], scaling relation in phase-separated colloidal dispersions [80], free energy differences [95], pressure tensor method for repulsive ellipsoids [90], hard spherocylinders [82], hard and soft ellipsoids [96], finite-size analysis for soft repulsive spherocylinders [87], capillary wave spectrum for repulsive ellipsoids [90], variational method [97], and step-function density profile [98], etc. For thermotropic LCs, the anisotropic Gay-Berne (GB) potential model [99] (refer sec. 2.5.1 for details) has been widely used to investigate the iso-nm interfacial properties [77, 91, 93]. The interfacial properties, such as interfacial width, interfacial tension, etc., might be influenced by the molecular interactions, capillary-wave undulations, coupled translational and rotational degrees of freedom [96] etc. For instance, the iso-nm interfacial tension was found to be increased with the aspect ratio (i.e., the ratio of diameters of molecular long and short axes) [89].

The surfaces and interfaces present in the system break the space isotropy and

promote a certain molecular alignment known as surface anchoring. The surface anchoring phenomenon is a crucial feature in the field of liquid crystal physics [82]. The surface anchoring effect is represented by the anchoring strength or energy and an angle (θ) between the preferred director orientation and normal to the surface or interface. The surface anchoring with $\theta=0^\circ$ and $\theta=90^\circ$ correspond to the homeotropic (or perpendicular) and planar (or parallel) anchoring, respectively [100]. If the director does not orient with planar nor homeotropic anchoring, then the only stable anchoring is the oblique one [101]. The tilt angle depends on the molecular symmetry rather than on the interactions type [97]. The iso-nm interfacial studies for different LC systems have resulted into planar [77, 78, 79, 86, 87, 94, 96, 97, 102], homeotropic [98, 102, 103] and oblique [84, 98, 101, 104] anchorings. The GB potential model with different sets of parameters such as $(\kappa, \kappa', \mu, \nu)$ equal to $(3, 5, 1, 3)$ [93] and $(4.4, 20, 1, 1)$ [91] have resulted into the planar anchoring at the iso-nm interface (Fig. 1.5). Depending upon the type of surface anchoring, the surface tension can be different because the free energy cost is different for the interfacial fluctuations in directions parallel and perpendicular to the director. The dependence of the interfacial tension on the tilt-angle is found to be due to the dependence of the interfacial width on the tilt-angle [80]. The interfacial tension as a function of the director orientation determines the surface preferred bulk molecular orientation. In most of the studies, the iso-nm interfacial tension (γ_{IN}) was found to be minimum for the planar anchoring [78, 79, 82, 86, 95]. However, some studies found the minimum interfacial tension at the tilt angle of $\pi/3$ [84, 98].

The interfacial anchoring can be modified by external magnetic or electric fields and by adding certain contributions to the intermolecular potential [93]. The homeotropic anchoring can be induced by selecting special boundary conditions or by preparing the initial nematic slab configuration with the normal orientation [88]. Onsager suggested that the iso-nm interface is flat, i.e., there are no capillary-wave fluctuations at the interface. However, Onsager's assumption is only valid for in-

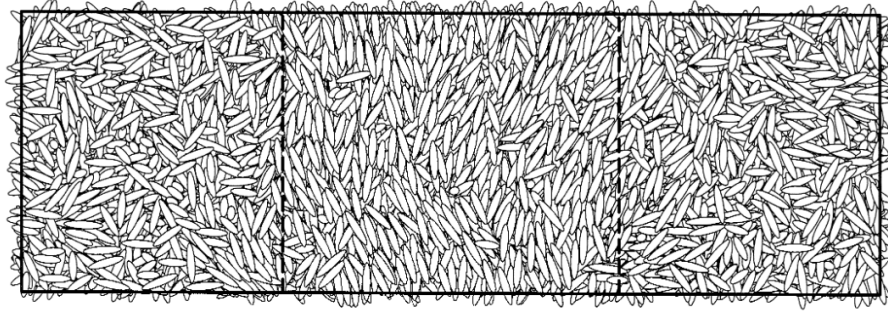


Figure 1.5: The isotropic-nematic interface formed in the GB liquid crystalline system. This image is taken from the work done by Martin A Bates, *Chem. Phys. Lett.* **288**, p. 209-215 (1998) [91]

finitely elongated particles [90]. The fluctuations in nematic liquid crystals have been well studied using Ericksen–Leslie theory, Ginzburg–Landau–de Gennes theory in the static case, and Langevin equations for the dynamic fluctuations [105].

1.5 Fluctuating interface

The knowledge of the dynamic fluctuations in the orientational tensor is essential to describe the nucleation rate for the nematic phase and to determine the capillary wave spectrum [105]. The capillary wave spectrum has been extensively studied in various iso-nm interfacial studies ([88, 89, 92], and refs. therein) and to estimate the iso-nm interfacial tension ([86, 90], and refs. therein). The fluctuations present at the interface increase the interfacial area with the cost of free energy [90], and these fluctuations are known as the capillary waves. The capillary waves lead to the broadening of the simulated density and nematic order parameter profiles, further resulting in the additional broadening when the average profile width is calculated by fixing the center of mass [89]. In the iso-nm interface, the capillary waves are found to be anisotropic due to stronger fluctuations in the director’s perpendicular direction than in parallel [90, 92]. The elastic interactions due to the nematic phase influence the capillary-wave spectrum and give rise to long-range interactions between the interfaces [92]. The long-range interfacial fluctuations result in long-

range elastic distortions in the director field. Further, the strong planar anchoring at the interface results in particles' orientations along the interface, which indicates the bending elasticity or flexible director regime (Fig. 1.6(a)) [86]. On the other hand, the strong bending rigidity does not allow the particles to orient along the interface. Consequently, there are two capillary wave regimes: the flexible director regime, which has isotropic capillary waves and is determined by the macroscopic surface tension. Another one is the stiff director regime, which has anisotropic capillary waves and is determined by the surface tension as a function of the orientation and strength of the wave vector. Hence, in the second case, the anisotropic interfacial tension dominates, and results in a stiff director field as observed in [86] (Fig. 1.6(b)). As in the computer simulation studies for interfacial fluctuations with

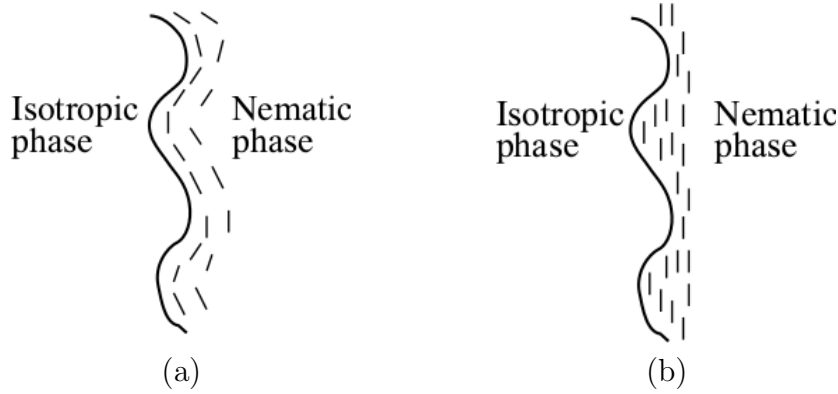


Figure 1.6: A sketch of the interfacial fluctuations or the capillary waves (adapted from the image shown by Wolfsheimer *et al.*, *Phys. Rev. E* **73**, p. 061703 (2006) [86]). The image (a) illustrates the strong interfacial anchoring in which the spectrum anisotropy is dominated by elasticity. The image (b) implies the strong bending rigidity in which the anisotropy of the interfacial tension influences the spectrum anisotropy

periodic boundary conditions, two parallel interfaces are formed. Therefore, an elongated simulation box should be used to avoid interfacial interactions and precisely measure the interfacial properties. Such a box configuration creates a significant separation between two interfaces, which are normal to the elongated dimension (to acquire the minimum interfacial area). However, the lateral dimensions might still have finite-size effects arising due to the capillary waves. Therefore, the lateral

dimensions should also be large enough to determine the capillary spectrum with long-wavelength limiting form [89]. The capillary waves can also be observed in the isotropic-smectic (iso-sm) interface, where there is a change in both positional and orientational order. However, the iso-sm interface is difficult to study experimentally because the free or solid surface present in a system affects the director alignment of the bulk smectic phase and thus influences the orientation at the iso-sm interface [91].

1.6 Isotropic-Smectic interface

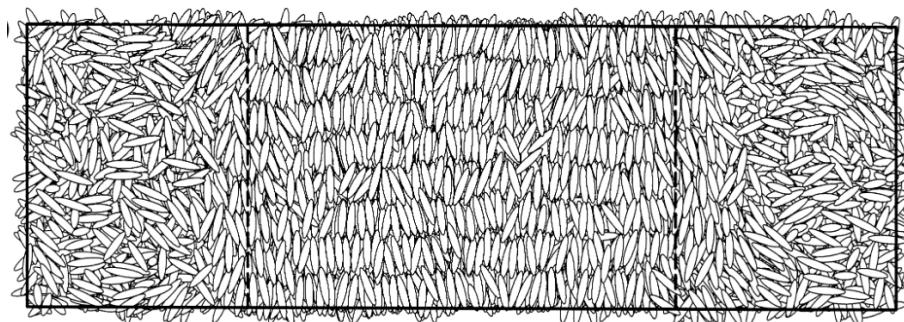


Figure 1.7: The isotropic-smectic interface formed in the GB liquid crystalline system and this image is taken from the work done by Martin A Bates, *Chem. Phys. Lett.* **288**, p. 209-215 (1998) [91]

For the iso-sm interface, does the anchoring depend only on the orientational correlation, or the translational correlations also play a role in determining the anchoring? In a study by M. A. Bates [91], the planar anchoring observed for isotropic-smectic A (iso-smA) interface exhibited no influence of the translational order present in the smectic-A (smA) phase on the average orientation at the interface. There, a narrow nematic layer between isotropic and smA phases was found due to the short-ranged orientational correlations and no translational correlations in the isotropic phase [91]. For the iso-sm interface, the interfacial thickness, spatial varying orientational order, and the translational order near the interface can be determined using the density and orientational order profiles [91]. The interfacial

width of the iso-smA interface is found to be larger than that of the iso-nm interface [91]. Therefore, it is expected that the nematic-smectic A (nm-smA) interfacial width would be very large, and thus, extensive systems would be needed to simulate the nm-smA interface [91]. Using MD simulations and GB potential model, the iso-smA interface has been studied with GB parameters (κ , κ' , μ , ν) equal to (3, 5, 1, 3) [93], and (4.4, 20, 1, 1) [91]. The growth pattern studies of smectic LCs from the isotropic phase showed that the shape of smA droplet depends on the interfacial tension anisotropy $\Delta\gamma = \gamma_{||} - \gamma_{\perp}$ (subscripts signify the parallel and perpendicular directions to the smectic layer normal) [106]. In these studies, the positive $\Delta\gamma$ indicates less interfacial tension along the smectic layers. Thus, smA droplets grew into an ellipsoidal shape during nucleation, with flat smectic layers normal to the ellipse's central axis. However, these layers were not normal to the interface everywhere, and hence, the layers bent to form a focal conic domain [106]. The focal conic structure and filamentary growth of the smA phase from the nematic phase are also observed [106]. On the other hand, the negative $\Delta\gamma$, in some compounds and binary mixtures, resulted in a cylindrical interface between smA droplet and nematic phase in which layers were parallel to the interface [106].

1.7 Nematic-Smectic B interface

Thermotropic LCs consisting of rod-like molecules exhibit complex patterns during the phase transitions [107]. For the equilibrium-shape measurements, the smectic-B (smB) phase is considered an appropriate choice due to relatively fast transport [108]. Experimentally, the nucleation of the nematic phase from smectic-B phase and vice versa has been investigated using various liquid crystalline materials showing the first-order nematic-smectic B (nm-smB) phase transition, and thus the nm-smB coexistence [108, 109, 110, 111]. These studies were performed in a quasi-two-dimensional geometry by bounding the LCs between the glass plates

[107,108,109,110,111]. There, the equilibrium shapes of nm and smB droplets were analyzed at different values of undercooling using various orientational combinations of two phases such as P(in P) (i.e., planar smB germ in planar nematic), P(in H) (i.e., planar smB germ in homeotropic nematic), H(in H) (i.e., homeotropic smB germ in homeotropic nematic), and H(in P) (i.e., homeotropic smB germ in planar nematic) [59, 107, 108, 109, 111, 112]. Depending upon the extent of undercooling, the morphology of planar smB germs in planar (P (in P)) or homeotropic (P (in H)) nematic changed from an initial elongated, rectangular shape (Fig. 1.8(a)) [112] with two long faceted sides (Fig. 1.8(b)) to butterfly-like shape (Fig. 1.8(c)) which finally formed dendrites with four-fold symmetry (Fig. 1.8(d)) [107, 108, 109, 111]. In the homeotropic case, the elastic deformations of the nematic phase, such as the splay-bend and twist types along the long and short interfacial edges, contributed to the surface energy [108,109,111]. In H (in H) configuration, the smB germs initially formed a circular shape which further went through a sequence of structures such as puddle-shaped [109], dense branching (Fig. 1.8(e)), dendrites, and petal-shaped at large undercooling [108,111]. The dendrites or dense branching have also been observed during crystallization in nematic material in columnar LCs comprising disk-like molecules [113,114]. However, it is rare to observe dendrites in rod-like thermotropic LCs [112]. In H (in P) configuration, an oval-shaped nm-smB interface

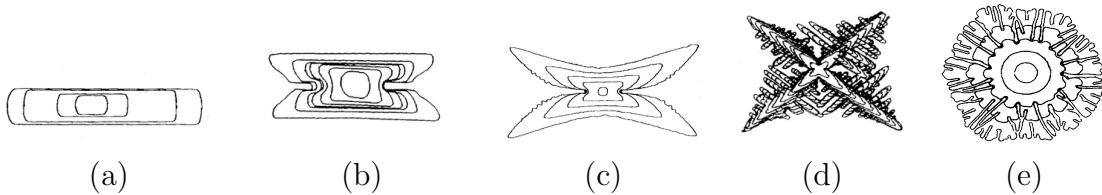


Figure 1.8: Different shapes of planar and homeotropic smectic-B germs in planar and homeotropic nematic phase in a quasi-two-dimensional geometry. These images are taken from the work done by Buka *et al.*, *Phys. Rev. E* **51**, p. 571-578 (1995) [107]

was observed [111] with the long faceted sides connected to the short convex sides without any cusp [115]. On the other hand, in the reverse case of heating the swiftly

grown smectic phase in such a quasi-two-dimensional geometry, the nucleation of nematic monodomains having non-faceted oval shape [109, 110] was observed with its major axis parallel to the smectic director [108]. In the above studies, the angular dependent (anisotropic) nm-smB surface tension $\sigma(\theta)$ (where θ tells the surface orientation) was determined using the classical Wulff construction [107, 108, 109, 111]. Apart from the nm-smB fronts [116, 117], the directional solidification has also been analyzed for smA-smB fronts [115, 118]. In addition to the homogeneous nucleation, the liquid crystalline system also undergoes several surface-ordering transitions when in contact with a surface [119]. The surface-induced phase transitions can result in the wetting phenomenon, which has attracted various theorists and experimenters.

1.8 Wetting phenomenon in LCs

The confined LCs instigate various fascinating surface and finite-size effects, and thus, they find important applications in designing various display devices, electrically controllable light-scattering devices, etc. [120, 121]. Therefore, LCs have become an interesting model system to examine the fundamental theories of wetting. The wetting properties might be dramatically affected by a subtle variation in the molecular interactions at the interfaces [122]. These interactions may result in melting or freezing of the surface before the corresponding bulk phase transition [123]. Some surface layers get disordered before the bulk melts, whereas the liquid crystalline surface layers get ordered above the bulk freezing [123]. The first microscopic picture of the ordering of the bulk isotropic phase at a solid interface was provided by B. M. Ocko [123] using x-ray reflectivity measurements. The isotropic or vapor phase often exhibits nematic or smectic-like order near the surface (Fig. 1.9) [124]. In the studies of the isotropic-air and nematic-air interfaces, the surface-induced smectic-like order has been observed [125]. These studies found discrete smectic layering with direct iso-smA phase transitions and continuous smectic layering with nm-smA phase tran-

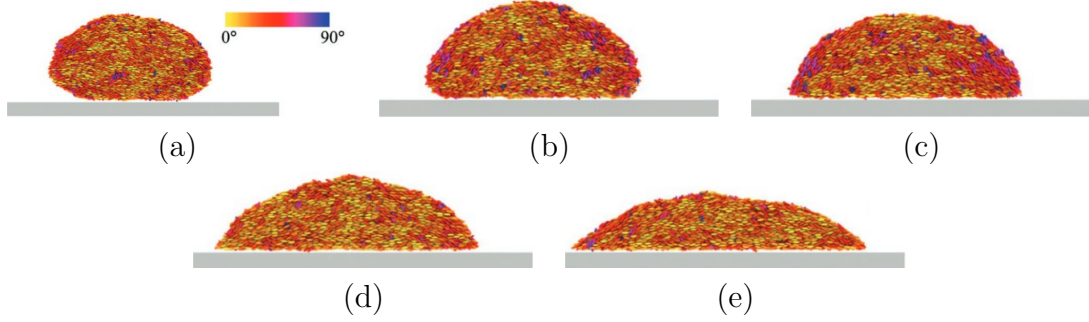


Figure 1.9: Wetting of the crystalline surface by equilibrated nematic nanodroplets from the vapor phase was observed by Vanzo *et al.*, *Soft Matter* **12**, p. 1610-1620 (2016) upon increasing affinity from (a) to (e). Vanzo *et al.* colored the particles differently to understand the tilt angle from the droplet's director [124]. The image is taken from [124]

sitions. The free surface-induced smA phase in the bulk isotropic phase was observed by adding single smectic layers near the surface through a series of discrete transitions [126]. These are called layering transitions, similar to the first-order phase transitions found in multilayer solid adsorption [127]. The layering transitions are found to be significantly broader at the solid interface than the air interface [123]. The effect of the glass plate on the nematic phase is found to be strongly attenuated due to the formation of a lamellar phase between them [128]. In this study, the main contribution to the surface energy was due to the interaction between the nematic and smectic layers. Upon cooling the nematic phase, the smectic ordering has been observed in a thin, planar-aligned liquid crystalline shell geometry [129]. Some studies on the smectic LCs found that the orientations of the surface and bulk molecules are very different [130, 131, 132, 133]. It could be due to the substantial effect of undulations on the bulk smectic LCs than on the surface smectic [127] such that the rise in free energy was more in bulk phase than in the surface phase. From nuclear magnetic resonance (*NMR*) measurements, the rate of exchanging the molecules between the surface layer and bulk was found to be significantly slower than that in the bulk [134]. This result suggested a local interaction between the surface layer and the surface. The liquid crystalline orientational order at the sur-

face has been investigated using various experimental techniques [60,134]. Different theoretical approaches have also studied the surface-induced layering phenomena above isotropic-smectic and nematic-smectic phase transitions [125,127,135].

1.9 Surface anchoring during wetting

Understanding of the surface-induced molecular order in LCs is crucial because of the significance of molecular alignment in the electro-optical devices, biological or chemical sensors [136]. The possible alignments of LCs near the surface are planar, homeotropic, and tilted, as shown in Fig. 1.10. The alignment near the surface is influenced by several factors, such as the type of coating material, the type of liquid crystal used, the method used to coat the substance, and the technique used to orient the surface material [125]. For instance, the surface roughness is found to have a pronounced effect on the angular distribution functions of particles near the surface [137]. Various theoretical approaches such as Landau-de Gennes,

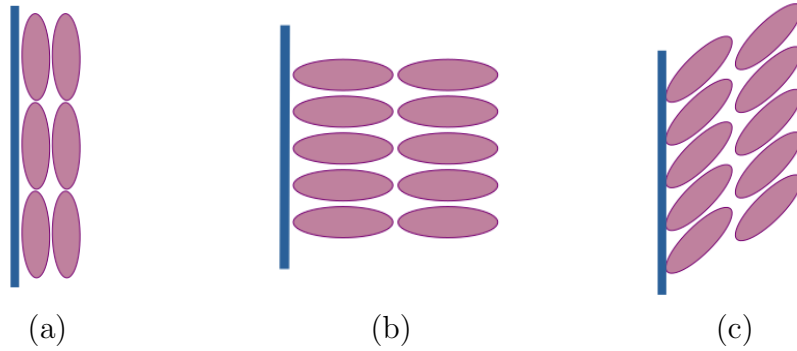


Figure 1.10: A pictorial representation of liquid crystalline particles on the surface with (a) planar, (b) homeotropic, and (c) oblique anchoring

Maier-Saupe, and molecular methods have been used to determine the orientational ordering of LCs near the surface [134]. There is a well understanding of the molecular features affecting the anchoring of the nematic phase in the vicinity of solid and free interfaces [128,138,139]. In the presence of a solid untreated surface, the excluded volume effect and van der Waals attractions of the surface are found to induce a

random planar alignment among the surface molecules [119]. At the cleaved graphite surfaces, LC molecules were arranged in an ordered array with their alignments in the plane of the surface [123]. Both the parallel and perpendicularly aligned surface-induced nematic phase have been observed for the bulk isotropic phase with different surface treatments [134]. Homeotropic anchoring is essential in appliances using vertically or hybrid aligned nematic cells [125]. The surfactants, such as sodium dodecyl benzene sulfonate (SDBS, LAS) or sodium dodecyl sulfonate (SDS), can induce the homeotropic anchoring [140]. Various experimental studies have observed the surface-induced layers with tilted or homeotropically aligned molecules [138]. In the presence of a wetting film of fluorocarbon perfluoromethylcyclohexane (PFMC), the homeotropically aligned smectic layering was observed, which further propagated into the bulk upon increasing the film thickness [133]. The smectic layers with homeotropic anchoring at a silicon surface (treated in different ways) were observed in nematic LC [125] and with a direct iso-smA transition [123,126]. The homeotropically aligned smectic layers have also been observed at the LC-air interface [132].

1.10 Complete or incomplete wetting

For confined systems, the liquid crystalline droplets of different shapes can be found depending upon the surface anchoring conditions [141] and the elastic constants of LCs [142]. Depending upon the droplet's interaction with the surface, a surface can be completely or incompletely wetted by the droplet (Fig. 1.11) [143,144,145]. The complete or incomplete wetting by the nematic phase is found to be dependent on the surface ordering field, and a surface pre-wetting transition may occur before the complete wetting [127]. Luckhurst *et al.* [146], and Pawlowska *et al.* [135] found the complete wetting by the nematic phase at an extremely high surface field. The complete or incomplete surface wetting by smA depends on the strength of the

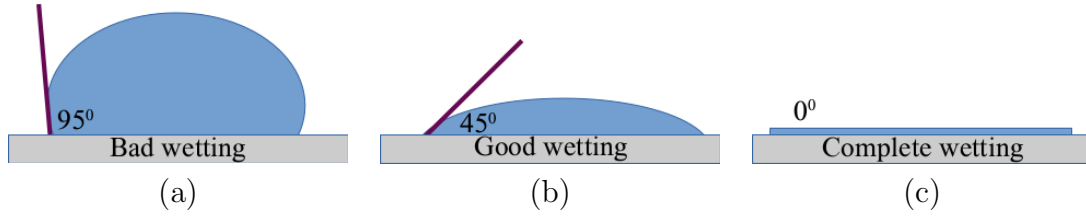


Figure 1.11: The pictorial illustration of the wetting behavior of droplets on the surface with the contact angle of (a) 95° for bad, (b) 45° for good, and (c) 0° for complete wetting (adapted from the work done by Baticados *et al.*, *Front. Environ. Sci.* **8**, p. 187 (2020) [143])

surface interaction potential [125]. Earlier theories suggested that if the nematic-smectic A (nm-smA) transition is first-order, the surface exhibits discrete smectic layers with incomplete wetting. Otherwise, if it is a second-order transition, the continuous smectic layering is observed with complete wetting [125]. To understand the smectic wetting, Pawlowska *et al.* [135] developed a lattice model based on the Ronis and Rosenblatt work [147, 148], which resulted in an incomplete wetting by up to four smectic layers. Out of four layers, three layers were added continuously, and the fourth layer was added through the first-order layering transition. Also, this model gave an inappropriate layering description that could not exhibit the physics of a real continuum system [127]. To sum up, with the literature review presented above, we found some gaps in studying the nucleation phenomenon in the liquid crystalline material, such as determining the properties of the nm-smB interface formed in unconfined LCs and of the interfaces formed in confined LCs. These gaps led to the motivation to accomplish the objectives of this thesis.

1.11 Motivation of the thesis

The homogeneous nucleation and wetting phenomena have been extensively studied in materials composed of spherical particles. Using various model systems for the spherical particles, the properties of different interfaces, such as liquid-vapor, solid-fluid, solid-surface, and fluid-surface, have been determined. However, in re-

SECTION 1.11: MOTIVATION OF THE THESIS

ality, the particles of the molecular materials are not only spherical. Hence, there is a need to study a system containing anisotropic or aspherical particles, such as liquid crystalline material. Due to the complex and sensitive phase diagram of LCs, the determination of interfacial properties in LC material results in interesting interfacial phenomenon, and thus, makes LCs to have various applications in different fields. For instance, the variation in the orientational order of molecules near the isotropic-nematic interface has numerous applications in functional materials, biosensors, etc. There are an enormous amount of studies on determining the properties of the isotropic-nematic, nematic-vapor and isotropic-vapor interfaces. Several works have also analyzed the morphology of isotropic and nematic droplets formed during the iso-nm coexistence. However, the interfacial studies are inadequate for the nematic-smectic B interface. A precise knowledge of the interfacial phenomenon in LCs, including the nm and smB phases, is required to develop better LC material using suitable processing methodologies. These interfacial studies are crucial because accurate estimation of the interfacial properties is indispensable for applications based on the crystal nucleation and growth phenomena. Therefore, there is a need to scrutinize the nm-smB phase coexistence and determine the properties of the nm-smB interface. In a quasi-two-dimensional geometry, the nm-smB phase coexistence has been well studied, which resulted in different shapes of the nm and smB droplets (as discussed earlier). However, as far as we know, the morphology of nm and smB droplets nucleated within the nm-smB coexistence has yet to be studied in a 3D system. Moreover, understanding the wetting behavior of an LC material confined by a surface is indispensable for various technological purposes, such as liquid crystal displays. Various studies have analyzed the behavior of an LC material in the vicinity of several surface potentials. However, to the best of our knowledge, the interfacial tension of an interface formed in an LC material confined by soft, smooth, and repulsive walls still needs to be determined. The importance of this kind of work arises in understanding the heterogeneous nucleation phenomenon when looked through the eye of Young's equation. In view of the above, the gaps

present in the interfacial studies have motivated us to carry out the work with the following objectives:

- Identify the coexistence region of liquid crystal phases.
- Calculate the interfacial properties of liquid crystalline interface.
- Characterise the nucleating droplet of liquid crystals.

Over experimental techniques, the computer simulations are helpful in understanding the nucleation phenomenon as the experimental observation of the rare nucleation event is challenging. Therefore, to accomplish the thesis objectives, we have used the LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) package that uses the molecular dynamics simulations technique. For the interaction between liquid crystalline particles, we have used the Gay-Berne potential model which is an anisotropic version of the spherical Lennard-Jones (LJ)(6-12) potential [149]. A detailed explanation of the MD technique, LAMMPS package, and GB potential are given in the next chapter. We will also discuss the nucleation phenomenon in detail, other potential models used to define the interaction, and the methods used to compute the interfacial properties.

Chapter 2

Theoretical formalism

2.1 Homogeneous and heterogeneous nucleation

Based upon the earlier works of Volmer and Farkas, a gas-to-liquid nucleation theory was developed by Becker and Doring. This theory was subsequently transformed by Zeldovich and the modified theory is now known as classical nucleation theory (CNT) [1,7,8,9,10,26]. CNT yields a basic but elegant description of the nucleation process, specifically the homogeneous nucleation (Fig. 2.1(a)). It is based on the unimolecular reaction kinetics and equilibrium statistical mechanics. CNT depicts that the free energy required to form a droplet can be written in terms of the droplet's volume and surface free energies [10,14]. Thus, for the nucleation event to take place, there is a need to overcome the free-energy barrier due to the competing surface and bulk-free energies (Fig. 2.1(b)). CNT states that a single nucleating droplet of the new stable phase expands by adding the molecules in a sea of the metastable mother phase. The size of this droplet must be greater than the critical size (i.e., the droplet with radius r^*) to compensate for the energy required to construct an interface between the two phases. After attaining the critical size, the droplet grows rapidly within the mother phase. The droplet and the metastable bulk phase are presumed to be separated by a sharp step-like interface. Based on the capillarity approximation, CNT treats the small nucleating clusters as the macroscopic regions

of space. CNT also assumes that the droplet's surface free energy is equivalent to the interfacial free energy per unit area of a flat macroscopic interface between the mother and nucleating phases. Therefore, the free energy required to form a droplet (or cluster) can be written as [21]

$$\Delta F_{hom} = F_S + F_V = \gamma A + \Delta f_V V. \quad (2.1)$$

where, the first one is the surface contribution term (F_S), with γ and A being the

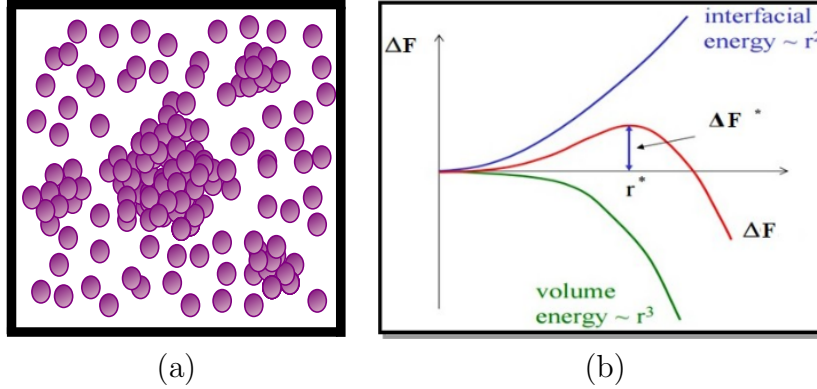


Figure 2.1: (a) A cartoon image shows the homogeneous nucleation in a system with periodic boundary conditions (without any wall). (b) The variation of surface, volume, and total free energy associated with the homogeneous nucleation with the droplet's size or radius (r)

interfacial tension, and droplet's surface area, respectively. The second term (F_V) is the free energy difference between the bulk droplet and the bulk mother phase. Here, $\Delta f_V = -\Delta\mu(\rho_1 - \rho_2)$ is the difference between the nucleating and mother phases' free energies per unit volume, and V is the droplet's volume. Here, $\Delta\mu = \mu - \mu_{coex}$ is the chemical potential difference relative to the phase coexistence value, and ρ_1 and ρ_2 are the bulk densities of the nucleating and the mother phases, respectively. The thermodynamically stable new phase has lower free energy per unit volume than the mother phase. However, due to the formation of an interface, the free energy increases by an amount proportional to the new phase's surface area. Hence, in most cases, the spherical critical nucleus of radius r is formed with $A=4\pi r^2$ and

SECTION 2.1: HOMOGENEOUS AND HETEROGENEOUS NUCLEATION

$V=(4/3)\pi r^3$. Therefore, the free energy required to create a spherical droplet or cluster becomes [4]

$$\Delta F_{hom}(r) = 4\pi r^2 \gamma + \frac{4\pi}{3} r^3 \Delta f_V. \quad (2.2)$$

where ΔF_{hom} depends on r or $n=\rho_{cl}V$ (which is the number of molecules constituting the droplet). Here, ρ_{cl} is the number density of the bulk droplet. The maximum value of ΔF_{hom} is ΔF_{hom}^* at $n=n^*$ which represents the thermodynamically defined critical droplet with the barrier height of $16\pi\gamma^3/3|\Delta f_V|^2$ [13]. The barrier height strongly depends on temperature and pressure. This height diverges near the phase coexistence region and when the driving force Δf_V approaches zero. Now by maximizing the Eq. 2.2 at the critical radius r^* , the free energy barrier ($\Delta F_{hom}(r^*)$ or ΔF_{hom}^*) comes out to be [4]

$$\Delta F_{hom}^* = (1/3)F_s(r^*). \quad (2.3)$$

Here, the subscript s in the surface free energy term ($F_s(r^*)$) indicates the spherical shape of the droplet. The free energy barrier (ΔF_{hom}^*) required for the spontaneous emergence of a critical nucleus is of the order of $20 \text{ } k_B T \leq \Delta F_{hom}^* \leq 200 \text{ } k_B T$. Hence, nucleation is a rare event compared to the thermal fluctuations that can be easily detected using scattering experiments. On the other hand, in heterogeneous nucleation, the surface or walls of the container aid the nucleation of a macroscopic droplet from the mother phase (Fig. 2.2(a)). To understand the heterogeneous nucleation, Thomas Young formulated an equation in 1895, and named it as the Young's equation [150]. This equation was further generalized by adding a line-tension term due to the three-phase contact line [151], which further modified the conventional heterogeneous nucleation theory [152, 153]. Young's equation characterizes the shape and behavior of the droplet where the droplet-mother interface

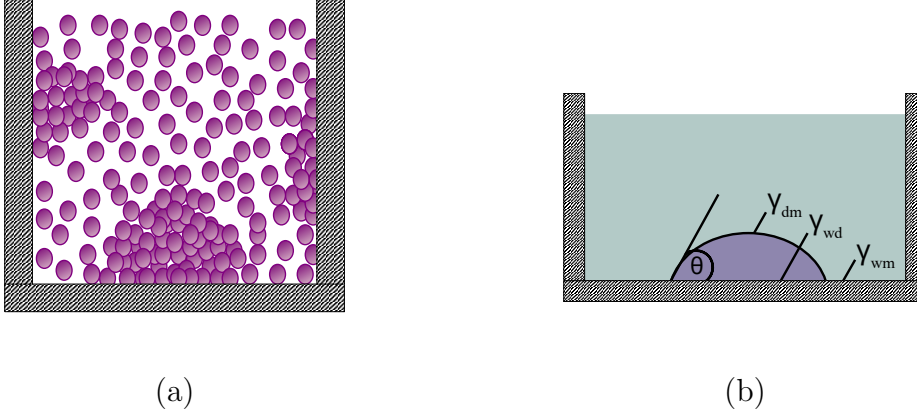


Figure 2.2: (a) A cartoon image shows the heterogeneous nucleation with the formation of droplets on the walls of an open container. (b) A reference image illustrates the contact angle (θ) and three interfacial tensions (γ_{wd} , γ_{dm} , and γ_{wm}) defined in Young's equation for a spherical cap-shaped droplet formed on the container walls

meets the surface (Fig. 2.2 (b)), and is defined as [4]

$$\gamma_{dm} \cos \theta = \gamma_{wm} - \gamma_{wd}. \quad (2.4)$$

where θ is the contact angle between the droplet and the wall, which determines the wetting behavior of the nucleus. It can be calculated by knowing the three competing interfacial tensions to form the droplet-mother (γ_{dm}), wall-droplet (γ_{wd}), and wall-mother (γ_{wm}) interfaces (Fig. 2.2(b)). For instance, $\theta = 0^\circ$ indicates the complete wetting with the layering structure of the droplet, $\theta = 90^\circ$ results in bad wetting, and $\theta = 180^\circ$ implies the homogeneous nucleation of a droplet without wetting the walls or surface. By considering the spherical geometry of the droplet (as per the CNT assumptions), the surface free energy [4] is given by

$$F_{s,hel} = F_{s,hom} f(\theta), \text{ where } f(\theta) = (1 - \cos \theta)^2 (2 + \cos \theta) / 4. \quad (2.5)$$

Interestingly, $f(\theta) = V_{spherecap} / V_{droplet}$, and Eq. 2.3 is also true for the heterogeneous case which gives

$$\Delta F_{het} = \Delta F_{hom} f(\theta). \quad (2.6)$$

SECTION 2.1: HOMOGENEOUS AND HETEROGENEOUS NUCLEATION

Eq. 2.6 implies that for heterogeneous nucleation, the free energy barrier is decreased (Fig. 2.3) by a Turnbull's factor of $f(\theta)$.

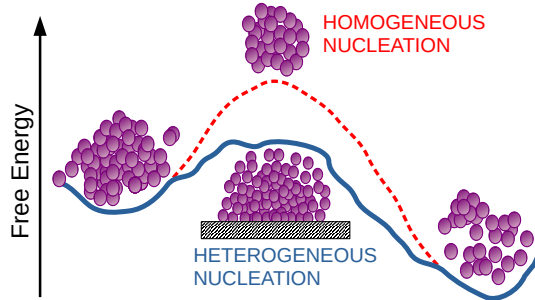


Figure 2.3: A sketch of the free energy barriers associated with the homogeneous and heterogeneous nucleation

The validation of CNT is being doubted in various studies [26]. As CNT suggested that the material at the core of the nucleus is a new bulk phase, and the surface free energy of a small nucleus is the same as that of an infinitely planar surface. However, these assumptions are questionable for very small nuclei, containing only 20-50 molecules, whose center is not in the thermodynamic limit, and if the interface formed is sharply curved. This theory is also not appropriate at a huge supersaturation ratio, leading to the small size of the critical nucleus and very large nucleation rate. Even, several studies also found a discrepancy between the results obtained from this theory and nucleation experiments [11]. Moreover, on the molecular scale, the vapor-liquid interface is diffuse rather than sharp, and thus the nucleation free energy (ΔF) can not be separated into bulk and interfacial terms [14]. These theoretical gaps result in an inadequate understanding of homogeneous nucleation. Furthermore, using experiments, the study of homogeneous nucleation of liquid droplets in supersaturated vapors is challenging because (i) of the small size and density of critical droplets such that they can only be detected by using light scattering methods [14, 154, 155] if they grow to a size much greater than the critical size. (ii) the heterogeneous nucleation at any nucleation site must be carefully avoided because the nucleation agents may dramatically decrease the free energy barrier, and thus, even a tiny amount of these agents may manipulate

the measurements [14]. For instance, the melting of 3D crystals does not have an associated free energy barrier in contrast to the freezing process because the bulk melting begins at a premelted surface, which vanishes the nucleation barrier [71]. Also, the nucleation rate is extremely sensitive to experimental conditions such as temperature, pressure, impurity concentrations, etc., because of its exponential dependence on rapidly changing free energies. Therefore, it is difficult to reproduce the experimental data and leads to large uncertainties in the theoretical estimation of the nucleation rate. In contrast, simulations play a crucial role in filling the gap between experiment and theory, and thus they have been successfully used in various nucleation studies [4]. The use of periodic boundary conditions helps to avoid the walls, and no other impurities occur during simulations. Moreover, simulations provide complete information about the atoms' positional coordinates, making the measurements possible at the nanoscale or single atomic scale. For the efficient study of the nucleation phenomenon using computer simulations, large systems must be simulated for a very long time as nucleation is a rare event for $\Delta F \gg k_B T$.

2.2 Molecular dynamics simulations technique

Computer simulations are performed using the molecular dynamics (MD) simulation technique for the thesis work. MD, developed by Alder and Wainwright in 1959 [156], is a computational approach to compute the static and dynamic properties of a classical system such as pressure, diffusion coefficient, etc. [157, 156, 158, 159, 160]. In the MD technique, the measurable quantity should be expressible in terms of positions and momenta of particles. This technique employs Newton's second law of motion to replicate the motion of individual particles within a physical system. Using the MD approach, the future state of a system can be predicted from its initial state, allowing us to observe how the system evolves over time and determine the trajectories and momentum of its atoms and molecules. Moreover, the results from experiments and MD simulations are comparable. During experiments, a physi-

SECTION 2.2: MOLECULAR DYNAMICS SIMULATIONS TECHNIQUE

cal sample of the material is initially prepared, and its various properties are then measured using various instruments. At times, these measurements are conducted while certain external parameters vary continuously. Similarly, an initial system configuration, akin to a sample, is set up in MD simulations. MD simulation steps are then carried out (by solving Newton's second equation of motion at different timesteps) to produce a series of sample configurations. This step is comparable to conducting experiments in a real physical setting. In the following step, various statistical ensemble-averaging techniques are applied to extract the system's macroscopic properties from the generated sample configurations. Therefore, the MD technique includes three steps to simulate a system [161]: Initialization, force calculation, and integration of Newton's equations of motion.

1. Initialization: Firstly, the system is initialized by defining the initial properties of per-atom and the whole system (or global). The global properties include temperature, timestep, density, etc. The per-atom properties include particles' positions, velocities, orientations, etc. Initially, the particles are positioned in a mechanically unstable lattice (sc, fcc, hcp, etc.), which quickly undergoes to another state. During this step, the atomic or molecular cores should not overlap. Then, the velocities following the uniform Gaussian distribution are assigned to the particles, which are further scaled so that the total momentum is zero. These velocities are also scaled to achieve the desired kinetic energy.
2. Force calculation: This step takes most of the time in MD simulations as the force acting on each particle, due to all its neighboring particles, is calculated. For instance, the force acting on particles in a Lennard-Jones fluid can be calculated as $\mathbf{F}(\mathbf{r}) = -dV_{LJ}(\mathbf{r})/dr \hat{\mathbf{r}}$ where

$$V_{LJ}(\mathbf{r}) = 4\epsilon_0 \left[\left(\frac{\sigma_0}{r} \right)^{12} - \left(\frac{\sigma_0}{r} \right)^6 \right]. \quad (2.7)$$

Therefore, the x-component of $\mathbf{F}(\mathbf{r})$ is

$$f_x(\mathbf{r}) = 24\epsilon_0 \left[2 \left(\frac{\sigma_0}{r} \right)^{12} - \left(\frac{\sigma_0}{r} \right)^6 \right] \frac{x}{r^2}. \quad (2.8)$$

Here, $\mathbf{r} = x\hat{\mathbf{i}} + y\hat{\mathbf{j}} + z\hat{\mathbf{k}}$ with $r = |\mathbf{r}|$ is the distance between two particles and $\hat{\mathbf{r}} = \mathbf{r}/r$, ϵ_0 is the potential well depth and σ_0 is the distance parameter where the potential is zero. For the force calculation in a system containing N particles with pairwise additive interactions, the $N(N-1)/2$ pair distances are evaluated by implementing the periodic boundary conditions.

3. Integrating equations of motion: After the force calculations, the particles' updated positions and velocities are computed by integrating Newton's second equation of motion. Various MD algorithms can be used to perform the calculations. One of them is the Verlet algorithm in which the updated particles' coordinates and velocity at timestep $t + \delta t$ can be computed, using Taylor's expansion and ignoring the higher powers, as

$$\mathbf{r}(t + \delta t) \approx 2\mathbf{r}(t) - \mathbf{r}(t - \delta t) + \frac{f(t)}{m} \delta t^2, \quad (2.9)$$

$$\mathbf{v}(t) = \frac{\mathbf{r}(t + \delta t) - \mathbf{r}(t - \delta t)}{2\delta t}. \quad (2.10)$$

Here, δt is the timestep size. Then, the velocity expression can be used to calculate the instantaneous kinetic energy, and instantaneous temperature as

$$T(t) = \frac{\sum_{i=1}^{\infty} m_i v_i^2(t)}{k_B N_f} \quad (2.11)$$

Here, N_f is the number of degrees of freedom, and v_i is the i^{th} particle's velocity. In reduced units, the Boltzmann constant (k_B) and particles' mass

SECTION 2.2: MOLECULAR DYNAMICS SIMULATIONS TECHNIQUE

(m) are taken to be unity. To calculate the particles' positions at further timesteps, the current positions are used as the old ones, and the new positions become the current ones. The current temperature, potential energy, and total energy are calculated at every timestep. This process is repeated for the required simulation duration. The Verlet algorithm is fast, area-preserving, time-reversible, and needs little memory, but is not accurate for long timesteps. In addition to the Verlet algorithm, there are other various MD algorithms to update the positions and velocities, such as Euler, Leap Frog, Velocity Verlet, Beeman, and velocity-corrected Verlet algorithms [156, 158, 161, 162, 163, 164, 165]. Conventionally, the total energy is conserved in MD; thus, the microcanonical ensemble (NVE) can be used for the simulations. In addition to NVE ensemble, the MD simulations can also be performed with a canonical ensemble (i.e., NpT or NVT) [166, 167] by using some temperature [168] and pressure control methods. The following briefly discusses different ensembles to be used in MD simulations.

2.2.1 Microcanonical ensemble (NVE)

A microcanonical ensemble describes all possible states of a system isolated from its surroundings, with no exchange of energy or mass. In such a system, both total energy and mass stay constant over time. During a microcanonical molecular dynamics simulation, energy fluctuates between potential energy (E_{pot}) and kinetic energy (E_{kin}), while the total energy ($E = E_{\text{kin}} + E_{\text{pot}}$) stays fixed. Notably, total energy is conserved when all forces in Newton's equations of motion are derived from the system's potential energy. Therefore, only systems with conservative forces can be represented as microcanonical ensembles.

2.2.2 Canonical ensemble (NpT and NVT)

The canonical ensemble is a statistical framework for systems interacting with a heat bath at a stable temperature. It permits energy exchange, leading to fluctuations in total energy, but the system’s mass stays constant. There are two types of canonical ensembles: constant volume (NVT) and constant pressure (NpT). NVE ensembles are simpler to simulate than NVT and NpT . As previously noted, when the system’s forces arise from inter-constituent potentials, its total energy remains constant, and microstates are generated by integrating Newton’s laws. However, if the system exchanges energy with its environment, integrating Newton’s laws alone is insufficient. Therefore, molecular dynamics (MD) simulations of NVT and NpT ensembles use specialized methods to control temperature and pressure.

Constant volume canonical ensemble (NVT)

This section provides a brief overview of some common methods employed in MD simulations for maintaining temperature at constant volume:

1. **Velocity Scaling: Isokinetics and the Berendsen thermostat:** In the isokinetic and Berendsen thermostat [169] scheme, the randomly chosen initial velocities of particles are rescaled to get the desired temperature. The thermostat in which kinetic energy remains constant, maintaining the system’s instantaneous temperature equal to the bath temperature, is called an isokinetic thermostat. To achieve some desired temperature T at a timestep, the velocities (Eq. (2.12)) are scaled by λ factor,

$$\frac{3}{2}Nk_B T = \frac{1}{2} \sum_i m_i v_i^2, \quad (2.12)$$

$$\lambda = \sqrt{(T/T(t))} \quad (2.13)$$

where $T(t)$ is the system’s actual temperature at a specific timestep t . This

SECTION 2.2: MOLECULAR DYNAMICS SIMULATIONS TECHNIQUE

thermostat can be used during initialization but not to simulate a canonical ensemble. Similarly, Berendsen thermostat [169] is a velocity scaling scheme in which a scaling factor is given by:

$$\lambda = \left[1 + \frac{\delta t}{\tau_T} \left(\frac{T}{T_0} - 1 \right) \right]^{\frac{1}{2}} \quad (2.14)$$

where T_0 is the set point temperature (i.e., the temperature of heat bath), δt is the timestep and τ_T is rise temperature. τ_T determines the system's coupling strength to the bath, with stronger coupling occurring at lower τ_T values. These velocity scaling methods do not preserve the accurate time evolution of canonical systems, making them unsuitable for MD simulations investigating system dynamics.

2. **Stochastic NVT thermostats:** The stochastic methods include Anderson, Langevin, and Dissipative Particle Dynamics (DPD) thermostats. In the Anderson thermostat [168, 170], the target temperature (T) is reached by randomly selecting particles and setting their velocities according to the Maxwell-Boltzmann (MB) distribution:

$$P(p) = \left(\frac{1}{2\pi m k_B T} \right)^{3/2} \exp \left(\frac{-p^2}{2m k_B T} \right). \quad (2.15)$$

The strategy of randomly selecting particles and assigning their velocities based on the MB distribution is designed to emulate the exchange of the system's energy with the bath, similar to random particle collisions with the bath wall. The coupling strength is governed by the collision frequency parameter ν , and the particles' velocities are updated at each MD timestep with $\nu\delta t$ probability.

In the Langevin thermostat, the particles receive stochastic forces, and the constant friction reduces their velocities [171]. The Dissipative Particle Dynamics (DPD) thermostat [172,173] can evaluate transport properties because pairwise stochastic and dissipative forces are added to all particles. As a consequence, momentum transport is conserved.

3. **Nosé-Hoover thermostat:** This thermostat is obtained when Hoover [174] further simplified the Nosé equations [175]. It is the most effective thermostat [174,176,177] which includes extensive Lagrangian formalism and there is no need to calculate stochastic forces or velocities. This method incorporates a fictitious coordinate (s) into the system's Hamiltonian. Physically, this coordinate generates a friction term $\xi = sp_s/Q$, regulating particle speed to achieve thermal equilibrium with the heat bath. The fictitious momentum p_s is associated with s , and Q serves an effective mass for s . The parameter Q regulates the system's coupling to the heat bath. The resulting equations of motion for i^{th} particle in an N -particle system become

$$\frac{d\mathbf{r}_i}{dt} = \mathbf{v}_i \quad (2.16)$$

$$\frac{d\mathbf{v}_i}{dt} = -\frac{1}{m_i} \frac{\partial U(\mathbf{r}^N)}{\partial \mathbf{r}_i} - \xi \mathbf{v}_i \quad (2.17)$$

$$\frac{d\xi}{dt} = \left(\sum_i m_i |\mathbf{v}_i|^2 - 3Nk_B T \right) / Q \quad (2.18)$$

$$\frac{d \ln s}{dt} = \xi \quad (2.19)$$

$$(2.20)$$

Constant pressure canonical ensemble (NpT)

Below, we briefly overview a few methods commonly used to regulate pressure in MD simulations. Maintaining constant pressure, known as barostating the system, is typically accomplished by varying the system's volume in response to its environment [161, 178, 179].

1. **Berendsen barostat:** This method employs a length scaling algorithm to adjust the system's volume, ensuring that the instantaneous pressure matches the target value set by the attached pressure bath. After integrating Newton's equations at a given timestep, the particle's positions ($\mathbf{r}$) and system size (i.e., the linear size of a cubic system, L) are updated as $\mathbf{r} \rightarrow \mu\mathbf{r}$ and $L \rightarrow \mu L$, respectively. Here, the scaling factor μ is

$$\mu = \left[1 + \frac{\delta t}{\tau_p} (p - p_0) \right]^{1/3} \quad (2.21)$$

where δt is the timestep, p_0 is the target or bath pressure, and τ_p is rise pressure. τ_p controls the coupling strength between the system and the pressure bath; a smaller τ_p value indicates stronger coupling. Similar to the Berendsen thermostat, these volume scaling methods fail to maintain accurate time evolution in canonical systems, making them unsuitable for MD simulations investigating system dynamics. Despite this limitation, the barostat is favored for equilibration due to its simplicity and computational speed.

2. **Andersen barostat:** This is an extended system technique, much like the Nosé-Hoover thermostat, where the system interacts with a pressure bath. A new degree of freedom is introduced in the equations of motion, simulating a piston that alters the system's volume. The piston, with mass Q , possesses both kinetic and potential energy. A lower Q induces faster volume fluctuations, whereas a higher Q results in slower oscillations [167]. A key limitation

of this method is that it permits only isotropic volume fluctuations. However, Parrinello and Rahman addressed this by enhancing the Andersen algorithm to allow for anisotropic box deformations [180, 181]. The Parrinello-Rahman barostat, with equations of motion resembling those of the Nosé-Hoover thermostat, can accurately reproduce the NpT ensemble when paired with the Nosé-Hoover thermostat.

3. **Nosé-Hoover barostat:** Nosé and Klein initially applied a method for molecular simulations similar to the Andersen barostat, which Hoover later refined into the widely known Nosé-Hoover barostat [178, 182]. However, the method's equations of motion were only valid for large systems. To overcome this, Martyna, Tuckerman, Tobias, and Klein (MTTK) proposed new equations of motion [183]. The MTTK barostat, an extended Nosé-Hoover thermostat, is often paired with it to obtain accurate NpT ensemble statistics.

2.3 LAMMPS

To accomplish our thesis objectives, the simulations are performed using the LAMMPS package, which uses the classical MD technique. The simulations are run with the canonical ensemble using the Nosé-Hoover thermostat and MTTK barostat in LAMMPS. Originally developed at Sandia National Laboratories U.S., LAMMPS is a Large-scale Atomic/Molecular Massively Parallel Simulator package [184, 185]. It is an open-source code available under GNU Public License Version 2 (GPLv2). LAMMPS currently contains source codes in C++, but the earlier versions were in F77 and F90. The simulations can be run on single and parallel processors using message-passing and spatial-decomposition techniques. Using different boundary conditions and interatomic potentials, it can simulate various model systems ranging from atomic, biological, solid-state, granular, or macroscopic systems. LAMMPS also includes short- and long-range interaction models and can simulate two- or three-dimensional model systems with a few or billions of particles.

Furthermore, one can easily modify or extend this package by adding new capabilities such as atomic potentials, boundary conditions, etc. LAMMPS has a host of commands to be used in an input script to prepare the desired system and execute the calculations. An inbuilt interpreter in LAMMPS reads the input script line by line. Hence, based on one's requirements, the input script is designed by including the following steps:

2.3.1 Initialization

The input script begins with an initialization step in which the system's macroscopic (i.e., global) and microscopic (i.e., per-atom) properties are defined. The first term to be declared is the system of units to measure the input and output quantities. The syntax to define the units is

```
units           style
```

where the **style** of units can be **real**, **lj**, **si**, **cgs**, etc. For our work, the **lj** units are used to make the quantities unitless by reducing them with the Lennard-Jones parameters (i.e., σ and ϵ). The results obtained with **lj** system of units are highly generalized. Therefore, using a specific material's σ and ϵ , our simulation results can be converted into actual values for that material. For instance, the reduced temperature can be converted into an actual one using the relation, $T = T^*\epsilon/k_B$. Here, the actual and reduced quantities are written without and with an asterisk (i.e., T and T^*), respectively. Further, the system's dimensionality is fixed by the **dimension** command. The box's periodic or non-periodic (fixed or shrink-wrapped) boundary conditions can be defined by the **boundary** command. The next step is to specify the initial configuration of particles, i.e., the type of lattice to define the particles' positions. This is done by using the following command

```
lattice         style scale keyword values
```

where **style** can be any of **sq**, **hex**, **sc**, **bcc**, **fcc**, etc. Here, **scale** is the scaling factor between lattice and simulation box, which is the reduced density in **lj** system

of units. Different keywords can also be defined to create a desired unit cell. After assigning the lattice sites to the particles, we need a region to create a simulation box, which can be done by using

`region` `ID style arguments keyword arguments`

where a user can define the region name as `ID`, and `style` can be any of the `block`, `cylinder`, `plane`, etc., with their arguments specified. Other region-related keywords can also be defined. Now, in the specified region, a box is created by using

`create_box` `N region-ID keyword value`

where `N` is the number of atom or particle types, `region-ID` is the region name and other optional keywords can also be defined. Further, the atomic properties, such as style, shape, size, mass, velocity, etc., can be defined by various commands. The style or shape of the particle is defined by using the command

`atom.style` `style arguments`

where `style` can be a `sphere`, `ellipsoid`, `dipole`, `electron`, etc., with the arguments specified for that particular style. We have used the ellipsoidal shape of the particles with their mass, size, and orientations defined by `set` command. Further, to assign velocities to the particles, we can use the velocity command as

`velocity` `group-ID style args keyword value`

where `style` can be `create`, `set`, `scale`, etc., with their arguments defined. The interaction between the particles is defined by a `pair_style` command whose syntax is

`pair_style` `style arguments`

Various pair styles are available in LAMMPS, such as `lj/cut`, `gayberne`, `tersoff`, `yukawa`, and so on. We have used the `gayberne` pair style with arguments of γ (shift for potential minimum), ν , μ , and cut-off parameters defined in GB potential (described later in detail). The pair coefficients of GB potential, i.e., well depth, relative well depths, and minimum effective particle radii, are defined by the `pair_coeff` command. We have run all the simulations with GPU using the `package gpu` command. The `gayberne` pair-style with GPU is available in LAMMPS. A `neighbor`

command can also be defined to construct the pairwise neighbor lists. Using a `variable` command, the variables can be defined to be used for evaluation during a simulation or later in the input script.

2.3.2 Simulation settings

After initializing the microscopic and macroscopic properties of the system, the next step is to specify other simulation settings, such as computing the system and per-atom properties, fixing the ensemble, timestep size during the run, etc. The `timestep` command can specify the timestep size to be used during the simulations. The `compute` command calculates global, local, and per-atom quantities. The `computes` do not perform computation but are invoked by other commands such as generating output in the dump file, calculating temperature for a thermostat fix, etc. The syntax of the `compute` command is

```
compute          compute-ID group-ID style arguments
```

where `compute-ID` is a user-assigned name, `group-ID` is the group of atoms to be included for the computation, and `style` can be any of the `property/atom`, `temp` (temperature), `extra/dof` (extra degrees of freedom), etc., with their arguments specified. Further, to update the atoms' positions and velocities, enforce boundary conditions, and fix the ensemble, a `fix` command is used whose syntax is

```
fix              ID group-ID style arguments
```

where `style` can be `nve/asphere`, `nvt/asphere`, `npt/asphere`, `wall/lj126`, etc., with their arguments defined. In our simulations, we have used `npt/asphere` and `nvt/asphere` which use the Nosé-Hoover barostat and thermostat to perform constant NpT and NVT integration.

2.3.3 Running the simulations

Once the system is initialized and simulation settings are done as desired, the simulations are run for a specified number of timesteps. For this, the `run` command is

used as

```
run                N keyword values
```

where `N` is the number of timesteps. Other keywords can also be defined here. Moreover, the current state of the simulation can be stored in binary files in every `N` timesteps using the `restart` command as

```
restart            N file1 file2
```

If one file name is specified (i.e., only `file1`), a series of filenames at all timesteps is created. However, the specification of two filenames (i.e., `file1` and `file2`) creates only two files, and LAMMPS toggles between them when successively writes into the restart files. We can use the restart files to continue the simulations from the same point where the previous run ends using the `read_restart` command.

2.3.4 Data collection

Data needs to be collected during the run to analyze the system's behavior and properties. The instantaneous thermodynamic output, such as pressure, temperature, density, energy, etc., can be printed on the screen and in log files by using the command

```
thermo_style       style arguments
```

To print the computes, fixes, and equal-style variables in the output files, they can be defined as `c_ID`, `f_ID`, and `v_name`, respectively (where `ID` is the user-defined name for computes and fixes). With a `thermo` command, the timesteps after which the quantities will be written in a log file or screen can be defined. Now, the instantaneous per-atom properties, such as positions, orientations, etc., can be printed in dump files using the `dump` command as

```
dump               ID group-ID style N file arguments
```

Here, the `style` has a long list of options available. For instance, with the `custom` style, we can print the positions (i.e., `x`, `y`, and `z`) and quaternions (i.e., `q[0]`, `q[1]`, `q[2]`, and `q[3]`), after every `N` timesteps. The `compute`, `fix`, and `dump` commands can be turned off by using `uncompute`, `unfix`, and `undump` commands.

More information about the commands and usage of LAMMPS can be found on the LAMMPS website (<https://docs.lammps.org>). For the present work, we have used the LAMMPS package to simulate the thermotropic liquid crystalline system to understand the interfacial phenomenon in LCs.

2.4 Liquid crystals

During liquid-to-solid transition, some mesomorphic phases exist whose properties are intermediate that of a liquid and a crystal, and are known as liquid crystals (LCs) [37, 42, 43, 44, 186]. LC material is composed of rod-like (elongated) [187] and disc-like shaped molecules. Depending on the phase transitions, there are different types of LCs such as metallotropic, lyotropic, and thermotropic. Lyotropic LCs are made up of organic molecules whose size and shape determine the properties of LCs. The lyotropic LCs undergo phase transitions when the temperature and concentration are varied [188, 189]. Metallotropic LCs are composed of organic and inorganic molecules and undergo phase transitions when the organic-inorganic composition ratio, concentration, and temperature are varied [190]. Thermotropic LCs consist of organic molecules and undergo phase transitions upon varying the temperature [43, 44, 100]. Apart from the isotropic, nematic, and smectic phases (shown earlier in Fig. 1.2), the thermotropic LCs also exhibit cholesteric and columnar phases [100]. The cholesteric phase, like the nematic phase, includes a differently aligned director in a regular fashion right through the medium. The columnar phase [191] comprises disc-like (discotic) molecules that are singled-dimensionally stacked to form cylindrical structures. LCs are everywhere in nature, such as cell membranes, living bodies, a few clays, soap and detergent solutions, etc. Liquid crystal technology is widely used in digital watches, calculators, optical imaging, mobiles, liquid crystal displays (LCDs), etc. They are used in lasers [192] and polymer dispersed liquid crystal (PDLC) sheets. Cholesteric LCs are used in medicines, electronics, and temperature

sensors such as thermometers. Over the years, computer simulation techniques have been used to study the thermotropic LCs using various model systems [193]. Most of the computer simulations of thermotropic LCs [39,40,41,99,186,194,195,196,197] have used the Gay-Berne (GB) pair potential [39,99,198,199].

2.5 Interaction potential models

2.5.1 Gay-Berne potential model

The GB potential model considers the molecules of an LC material as ellipsoids of revolution having a single-site representation in terms of the positions of their centers of masses. The GB potential depends on the intermolecular separation as well as the molecular orientations (Fig. 2.4(a)). The GB potential energy between two ellipsoidal molecules, i and j with their respective unit orientation vectors $\hat{\mathbf{u}}_i$ and $\hat{\mathbf{u}}_j$, is defined as

$$U_{ij}^{GB}(\mathbf{r}_{ij}, \hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j) = 4\epsilon(\hat{\mathbf{r}}_{ij}, \hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j)(R^{-12} - R^{-6})$$

$$\text{where, } R = \frac{r_{ij} - \sigma(\hat{\mathbf{r}}_{ij}, \hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j) + \sigma_0}{\sigma_0} \quad (2.22)$$

Here, $\mathbf{r}_{ij}$ is the separation vector between two molecules i and j with magnitude r_{ij} and unit vector $\hat{\mathbf{r}}_{ij} = \frac{\mathbf{r}_{ij}}{r_{ij}}$, σ is the molecular shape parameter and ϵ is the interaction strength parameter. The constant σ_0 is the particle's diameter along its minor axis. For a particular molecular orientation, the distance where the interaction strength vanishes is defined by σ , which is given by

$$\sigma(\hat{\mathbf{r}}_{ij}, \hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j) = \sigma_0 \left[1 - \frac{\chi}{2} \left\{ \frac{\{(\hat{\mathbf{u}}_i + \hat{\mathbf{u}}_j) \cdot \hat{\mathbf{r}}_{ij}\}^2}{1 + \chi(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j)} + \frac{\{(\hat{\mathbf{u}}_i - \hat{\mathbf{u}}_j) \cdot \hat{\mathbf{r}}_{ij}\}^2}{1 - \chi(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j)} \right\} \right]^{-\frac{1}{2}} \quad (2.23)$$

SECTION 2.5: INTERACTION POTENTIAL MODELS

where $\chi = (\kappa^2 - 1)/(\kappa^2 + 1)$. Here, the aspect ratio κ is a measure of the ratio of the molecular diameters along the major axis (σ_{ee}) and the minor axis ($\sigma_{ss} = \sigma_0$) such that $\kappa = \sigma_{ee}/\sigma_{ss}$. The aspect ratio determines the anisotropy in repulsive forces and affects the system's ability to get an orientationally ordered phase. It also tells the difference in attractive well depths between sidewise and crossed configurations of a pair of particles. The interaction strength ϵ , is given by

$$\epsilon(\hat{\mathbf{r}}_{ij}, \hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j) = \epsilon_0 [\epsilon_1(\hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j)]^\nu [\epsilon_2(\hat{\mathbf{r}}_{ij}, \hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j)]^\mu, \quad (2.24)$$

$$\epsilon_1(\hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j) = [1 - \chi^2(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j)^2]^{-1/2}, \quad (2.25)$$

$$\epsilon_2(\hat{\mathbf{r}}_{ij}, \hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j) = 1 - \frac{\chi'}{2} \left[\frac{\{(\hat{\mathbf{u}}_i + \hat{\mathbf{u}}_j) \cdot \hat{\mathbf{r}}_{ij}\}^2}{1 + \chi'(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j)} + \frac{\{(\hat{\mathbf{u}}_i - \hat{\mathbf{u}}_j) \cdot \hat{\mathbf{r}}_{ij}\}^2}{1 - \chi'(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j)} \right] \quad (2.26)$$

where $\chi' = (\kappa'^{1/\mu} - 1) / (\kappa'^{1/\mu} + 1)$ and ϵ_0 sets the overall energy scale. The parameter κ' is the ratio of the potential depths when the molecules interact sidewise (ϵ_{ss}) and when they interact end-to-end (ϵ_{ee}) i.e. $\kappa' = \epsilon_{ss}/\epsilon_{ee}$. This parameter influences the formation of a smectic phase. The exponents μ and ν are the adjustable parameters that control the anisotropy in ϵ and thus can alter the GB phase diagram. They influence the nematic and smectic formation due to the attractive anisotropic forces [200]. The set of these four parameters $(\kappa, \kappa', \mu, \nu)$ characterizes each member of the GB potential family. A lowest molecular elongation is required to obtain thermodynamically stable fluid phases possessing orientational order. Similarly, the lowest energetic-anisotropy is needed to achieve spatially inhomogeneous fluid phases. Both of these minima are partially associated with each other. Depending upon the choice of parameters, the model system can be prolate (rod-like if $\kappa > 1$) or oblate (disc-like if $\kappa < 1$) molecules. Most real mesogens are rod-like [202] whose constituent molecules must have an aspect ratio equal to or greater than 3 : 1 [200]. Therefore, we have chosen ellipsoids of a 3 : 1 aspect ratio, which are comparatively easier to simulate than ellipsoids of a higher

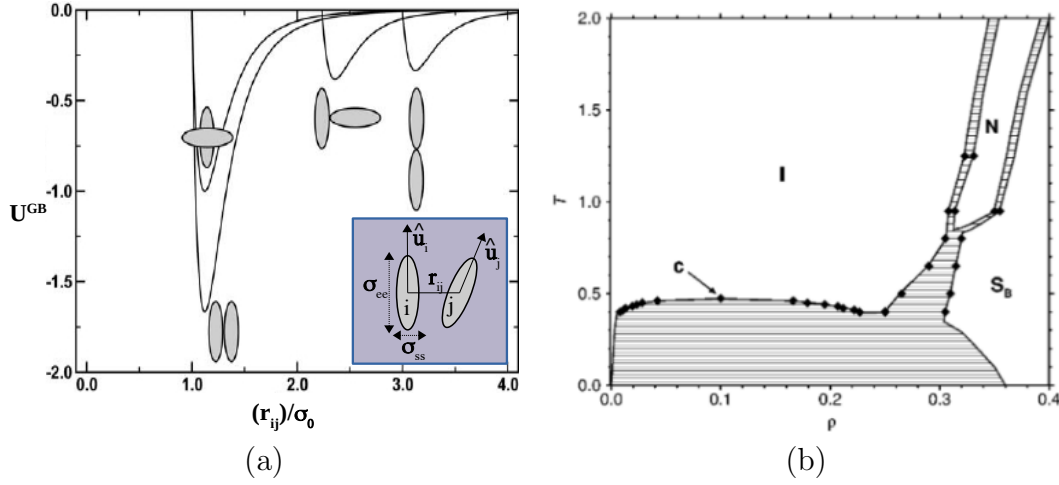


Figure 2.4: (a) The Gay-Berne interaction potential between molecules orienting in different configurations, i.e., side-by-side, end-to-end, t-shaped, and crosswise. The image is taken from the work done by Razo *et al.*, *Soft Matter*, **7**, p. 6828 [201]. (b) The Gay-Berne phase diagram exhibiting the isotropic (I), nematic (N), and smectic-B (S_B) phases for (3, 5, 2, 1) set of parameters, where c is the vapor-liquid critical point. The image is taken from the work done by Brown *et al.*, *Phys. Rev. E*, **57**, pp. 6685-6699 (1998) [186]

aspect ratio. To understand the interfacial properties, we must know the GB phase diagram. Various extensive studies have been done to report the phase diagram with different GB parameters [38, 199, 200, 203, 204]. Here, we have used the (3, 5, 2, 1) GB parameters, which have been extensively studied using computer simulations [36, 38, 40, 41, 186, 205, 206] and theoretical approaches [207, 208]. In the reported phase diagram of GB LCs with cut-off radius of $4\sigma_0$, the (3, 5, 2, 1) parameters resulted in a rich phase diagram with a clear identification of isotropic, nematic, and smectic-B phases (Fig. 2.4(b)) [186]. Hence with these parameters, there is a possibility of isotropic-nematic, isotropic-smectic B, and nematic-smectic B coexistence. All the thermodynamic quantities considered in our work are taken dimensionless in terms of molecular units of length σ_0 , energy ϵ_0 , and mass m_0 . The dimensionless forms of these quantities are: energy $U^* = U/U_0 = U/\epsilon_0$, temperature $T^* = T/T_0 = T/(k_B^{-1}\epsilon_0)$, number density $\rho^* = \rho/\rho_0 = (N/V)/\sigma_0^{-3}$, pressure $P^* = P/P_0 = P/(\epsilon_0\sigma_0^{-3})$, and time $t^* = t/t_0 = t/(\epsilon_0^{-1}\sigma_0^2m_0)^{1/2}$. They can be converted into

dimensional forms using the typical values of molecular units. For instance, $\sigma_0 = 5 \times 10^{-10}m$ (8CB mesogen's width [209]), $\epsilon_0 = 1.4 \times 10^{-21}J$ (using isotropic-nematic transition temperature, $k_B T_{NI}$ of 8CB), $m_0 = 4.8 \times 10^{-22}kg$. The derived units of time is $t_0 = 0.3$ ns, and pressure is $P_0 = 112$ bar [124]. Further, to study the confined GB system, the GB fluid is constricted by applying two soft, smooth, and repulsive walls at lower and higher z -edges of the simulation box (Fig. 2.6). The interaction between GB molecules and walls is defined by Weeks-Chandler-Anderson [210,211] potential.

2.5.2 Weeks-Chandler-Anderson potential

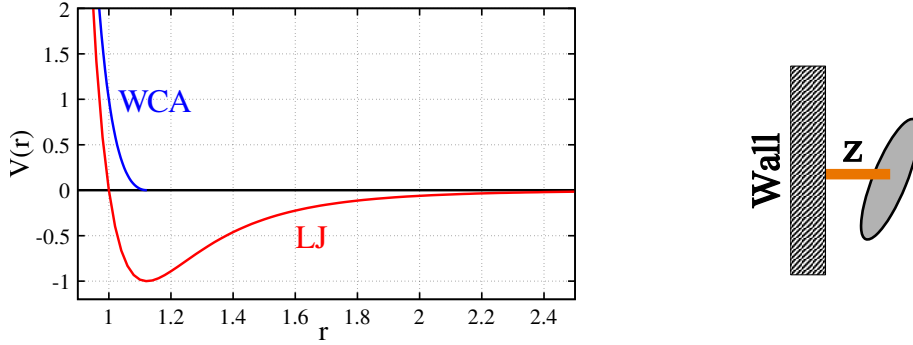


Figure 2.5: The soft, smooth, and repulsive Weeks-Chandler-Anderson (WCA) interaction potential between the wall and particle.

Weeks-Chandler-Anderson (WCA) potential is a truncated and shifted Lennard-Jones (6-12) potential (Fig. 2.5). The WCA interaction potential between the wall and a particle situated at z distance from the wall is given by

$$\begin{aligned}
 V_{WCA}(z) &= 4\epsilon_W \left[(\sigma_W/z)^{12} - (\sigma_W/z)^6 + \frac{1}{4} \right] & 0 \leq z \leq \sigma_W 2^{1/6}, \\
 &= 0 & \text{otherwise.} \quad (2.27)
 \end{aligned}$$

The strength and range of this potential are ϵ_W and σ_W , respectively. We have chosen the WCA form of soft repulsive potential for computational convenience.

This potential has been used to model the semiflexible polymers [212], investigate the behavior of the confined soft-repulsive nanorings [213], the interfacial properties of confined hard spheres [214], and colloid-polymer mixtures [215]. The main aim of our present thesis is to compute the properties of an interface formed between two phases of GB LCs (without any confinement), and the interface formed between GB LC and WCA wall (with confinement). To compute the interfacial properties, we have used the capillary wave theory and pressure tensor method for an unconfined and confined GB LC system, respectively.

2.6 Computation of the interfacial properties

2.6.1 Capillary wave theory (CWT)

The surface free energy or surface tension is an extensive quantity that defines the properties of a surface. Therefore, its determination is significant in the statistical thermodynamical treatment of surfaces [216,217]. In 1894, the classic Van der Waals theory [218] first predicted the existence of infinitely planar and intrinsic interfaces between two phases. This theory used the density profile to characterize the interface and determine the surface properties. Over the years, various approaches have been used to determine the surface properties, each having its own benefits and drawbacks [216, 219, 220, 221, 222, 223, 224, 225, 226]. In a system with finite size and at finite temperature, the interface is never sharply defined. Due to thermal fluctuations, the particles near the interface constantly find their surroundings change, leading to interfacial undulations that cost free energy. Such thermal undulations of the interface are known as capillary waves. The capillary waves have been studied in various systems using experiments, theoretical methods, and computer simulations [227,228]. In soft matter, it is easy to analyze the capillary waves because of their larger amplitudes compared to simple fluids, low interfacial tensions, large particle length scales, and comparable mass densities of coexisting phases.

SECTION 2.6: COMPUTATION OF THE INTERFACIAL PROPERTIES

Smoluchowski first anticipated the capillary waves [229], which were later given a theoretical framework known as capillary wave theory [228, 230, 231]. CWT, based on finite-size effects, only applies to a non-faceted interface. Using CWT, the interfacial behavior has been studied for various model systems such as hard spheres [232], nickel [233], polymer mixtures [234], colloid-polymer mixtures [235], metallic mixtures [236], Ising Model [237], and Asakura-Oosawa model [86, 88, 227, 228].

According to CWT, the mean-squared interfacial width (w), which depends on the intrinsic width (w_0) and cut-off parameter (l), diverges logarithmically with the lateral size ($L = L_x$) as

$$w^2 = w_0^2 + \frac{k_B T}{4\tilde{\gamma}} \ln(L) - \frac{k_B T}{4\tilde{\gamma}} \ln(l). \quad (2.28)$$

The cut-off parameter is there because CWT only accounts for the interfacial fluctuations having wavelengths larger than the typical interfacial width. In Eq. (2.28), $\tilde{\gamma}$ is the interfacial stiffness [238] which is related to the interfacial tension (γ) as $\tilde{\gamma} = \gamma + \partial^2 \gamma / \partial \theta \partial \psi$. Here, the second term ($\partial^2 \gamma / \partial \theta \partial \psi$) is the free energy required to change the local orientation of the smectic phase, where θ and ψ are the angles between the interface normal and two orthogonal directions [239, 240]. The term $\partial^2 \gamma / \partial \theta \partial \psi$ disappears if both the phases are isotropic at the interface, as in the case of the liquid-gas interface.

2.6.2 Pressure tensor (PT) method

The physical properties across an interface in inhomogeneous systems change sharply within a few molecular lengths [241]. These quantities are both anisotropic and non-uniform. The pressure tensor is one of these physical quantities which can characterize the interface mechanically. The pressure tensor is negative of the microscopic averaged stress tensor of an equilibrated fluid. The fluid pressure includes a well-

defined kinetic part due to molecules' linear momentum and a configurational part due to intermolecular central forces. However, the configurational part in an inhomogeneous fluid is not straightforward. This is due to the ambiguity in choosing where the intermolecular force is acting and which molecular pairs contribute to the stress across any microscopic surface area. Kirkwood first implicitly realized this uncertainty and found its two different forms with Buff [219] and Irving [242]. They acquired a formal treatment by probing the pressure over a planar surface. Later, it was explicitly described by Harasima [243], restated by Ono and Kondo [244], and its implications were explored in various works [245, 246].

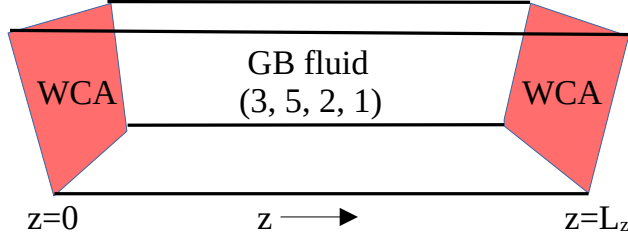


Figure 2.6: A reference image of a cuboidal box containing GB (3, 5, 2, 1) fluid confined by two WCA walls at the left and right z -edges of the box

The confinement of a fluid by a planar wall (say, normal to the z -direction as shown in Fig. 2.6) results in a wall-fluid interface whose interfacial tension can be calculated by using the pressure tensor (PT) method [214]. This method includes two non-zero pressure tensor components, i.e., the normal (P_N) and tangential (P_T) pressure. For the confined system, these pressure tensor components, apart from the kinetic and configurational part, also include the contribution from the wall-fluid interaction. The wall-fluid interaction potential acts only in the normal direction; therefore, it only contributes to the normal component of pressure, not the transverse component. Also, the kinetic contribution to P_N and the number density profile are proportional to each other [247]. For symmetrical planar interface, the transverse components are $P_T(z) = (P_{xx}(z) + P_{yy}(z))/2$ and $P_N(z) = P_{zz}(z)$. The pressure P of a system containing N particles in a volume V and at a temperature T is given

SECTION 2.6: COMPUTATION OF THE INTERFACIAL PROPERTIES

by [248, 249]

$$P = \rho k_B T + \frac{1}{3V} \left\langle \sum_i \sum_{j>i} \mathbf{r}_{ij} \cdot \mathbf{f}_{ij} \right\rangle. \quad (2.29)$$

For systems confined by planar surfaces, the pressure tensor is a function of distance z from the planar surface. According to the Irving-Kirkwood (IK) approximation [242, 247, 250, 251], the potential or virial part of the pressure tensor $P^U(z)$ can be written as

$$P^U(z) = -\frac{1}{2A} \left\langle \sum_i \sum_{j>i} \mathbf{r}_{ij} \cdot \mathbf{f}_{ij} \frac{1}{|z_{ij}|} \Theta\left(\frac{z - z_i}{z_{ij}}\right) \Theta\left(\frac{z_j - z}{z_{ij}}\right) \right\rangle. \quad (2.30)$$

For aspherical particles, the intermolecular forces include the configurational ($\mathbf{r}$) and the orientational ($\hat{\mathbf{u}}$) contributions [252]. Now, the force between two aspherical particles i and j having three orthonormal principal axes $m = 1, 2, 3$, can be calculated as [252]

$$\mathbf{f}_{ij} = -\frac{\partial U}{\partial \mathbf{r}} = -\frac{\partial U}{\partial r_{ij}} \frac{\partial r_{ij}}{\partial \mathbf{r}} - \sum_m \left\{ \frac{\partial U}{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_i)} \frac{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_i)}{\partial \mathbf{r}} + \frac{\partial U}{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_j)} \frac{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_j)}{\partial \mathbf{r}} \right\}, \quad (2.31)$$

where the intermolecular separation and the orientational unit vectors are

$$\mathbf{r} = x_{ij} \hat{\mathbf{i}} + y_{ij} \hat{\mathbf{j}} + z_{ij} \hat{\mathbf{k}}, \text{ and } r^2 = r_{ij}^2 = x_{ij}^2 + y_{ij}^2 + z_{ij}^2, \quad (2.32)$$

$$\hat{\mathbf{u}}_i = u_{ix} \hat{\mathbf{i}} + u_{iy} \hat{\mathbf{j}} + u_{iz} \hat{\mathbf{k}}, \text{ and } \hat{\mathbf{u}}_j = u_{jx} \hat{\mathbf{i}} + u_{jy} \hat{\mathbf{j}} + u_{jz} \hat{\mathbf{k}} \quad (2.33)$$

$$\begin{aligned}
\frac{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_i)}{\partial \mathbf{r}} &= \frac{1}{r_{ij}} \hat{\mathbf{u}}_i^\perp = \frac{1}{r_{ij}} \{\hat{\mathbf{u}}_i - (\hat{\mathbf{u}}_i \cdot \hat{\mathbf{r}}) \hat{\mathbf{r}}\} = \frac{1}{r_{ij}} \left\{ \hat{\mathbf{u}}_i - \left(\hat{\mathbf{u}}_i \cdot \frac{\mathbf{r}}{r_{ij}} \right) \frac{\mathbf{r}}{r_{ij}} \right\} \\
&= \frac{1}{r_{ij}} \{ (u_{ix} \hat{\mathbf{i}} + u_{iy} \hat{\mathbf{j}} + u_{iz} \hat{\mathbf{k}}) - \frac{1}{r_{ij}^2} (u_{ix} x_{ij} + u_{iy} y_{ij} + u_{iz} z_{ij}) \\
&\quad (x_{ij} \hat{\mathbf{i}} + y_{ij} \hat{\mathbf{j}} + z_{ij} \hat{\mathbf{k}}) \}. \tag{2.34}
\end{aligned}$$

$$\text{Hence, } \left(\frac{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_i)}{\partial \mathbf{r}} \right)_x = \frac{1}{r_{ij}} \{ u_{ix} - \frac{1}{r_{ij}^2} (u_{ix} x_{ij} + u_{iy} y_{ij} + u_{iz} z_{ij}) x_{ij} \}, \tag{2.35}$$

$$\left(\frac{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_i)}{\partial \mathbf{r}} \right)_y = \frac{1}{r_{ij}} \{ u_{iy} - \frac{1}{r_{ij}^2} (u_{ix} x_{ij} + u_{iy} y_{ij} + u_{iz} z_{ij}) y_{ij} \}, \tag{2.36}$$

$$\left(\frac{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_i)}{\partial \mathbf{r}} \right)_z = \frac{1}{r_{ij}} \{ u_{iz} - \frac{1}{r_{ij}^2} (u_{ix} x_{ij} + u_{iy} y_{ij} + u_{iz} z_{ij}) z_{ij} \}. \tag{2.37}$$

In our case, we considered only $m = 3$ in Eq. (2.31), i.e., the axis along the longest diameter of the ellipsoid. According to Irving-Kirkwood approximation [242, 247, 250, 251], the normal and tangential components of pressure tensor in the case of aspherical particles, due to kinetic and intermolecular (between a pair of ellipsoids i and j) forces' contributions, are:

$$\begin{aligned}
P_N^{IK}(z) &= \rho(z) k_B T - \frac{1}{A} \left\langle \sum_i \sum_{j>i} \left[\frac{|z_{ij}|}{r_{ij}} \frac{\partial U}{\partial r} + \frac{z_{ij}}{|z_{ij}|} \left\{ \frac{\partial U}{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_i)} \left(\frac{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_i)}{\partial \mathbf{r}} \right)_z + \right. \right. \right. \\
&\quad \left. \left. \frac{\partial U}{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_j)} \left(\frac{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_j)}{\partial \mathbf{r}} \right)_z \right\} \right] \Theta \left(\frac{z - z_i}{z_{ij}} \right) \Theta \left(\frac{z_j - z}{z_{ij}} \right) \right\rangle, \tag{2.38}
\end{aligned}$$

SECTION 2.6: COMPUTATION OF THE INTERFACIAL PROPERTIES

$$\begin{aligned}
P_T^{IK}(z) = & \rho(z)k_B T - \frac{1}{2A} \left\langle \sum_i \sum_{j>i} \left[\frac{x_{ij}^2 + y_{ij}^2}{|z_{ij}|r_{ij}} \frac{\partial U}{\partial r} + \right. \right. \\
& \frac{1}{|z_{ij}|} \left[\frac{\partial U}{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_i)} \left\{ x_{ij} \left(\frac{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_i)}{\partial \mathbf{r}} \right)_x + y_{ij} \left(\frac{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_i)}{\partial \mathbf{r}} \right)_y \right\} + \right. \\
& \left. \left. \frac{\partial U}{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_j)} \left\{ x_{ij} \left(\frac{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_j)}{\partial \mathbf{r}} \right)_x + y_{ij} \left(\frac{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_j)}{\partial \mathbf{r}} \right)_y \right\} \right] \right] \right\rangle \\
& \Theta \left(\frac{z - z_i}{z_{ij}} \right) \Theta \left(\frac{z_j - z}{z_{ij}} \right) \rangle. \tag{2.39}
\end{aligned}$$

where A is the interfacial area. Here, the first term in the virial part contains the derivative of potential energy (U) with respect to r (or r_{ij}) and second term involves the derivative of U with respect to $(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}})$. To calculate the pressure tensor components, we have to calculate the derivatives of the GB potential. Now, the GB potential [99] between two particles i and j is

$$U(\mathbf{r}, \hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j) = 4\epsilon(\hat{\mathbf{r}}, \hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j) \left[\left\{ \frac{\sigma_0}{r_{ij} - \sigma(\hat{\mathbf{r}}, \hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j) + \sigma_0} \right\}^{12} - \left\{ \frac{\sigma_0}{r_{ij} - \sigma(\hat{\mathbf{r}}, \hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j) + \sigma_0} \right\}^6 \right]. \tag{2.40}$$

To simplify the calculations, a function is defined as [40, 253]

$$g(X) = 1 - \frac{X}{2} \left\{ \frac{(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_i + \hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_j)^2}{1 + X(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j)} + \frac{(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_i - \hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_j)^2}{1 - X(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j)} \right\} \tag{2.41}$$

$$= 1 - \frac{X}{2r_{ij}^2} \left\{ \frac{(\mathbf{r} \cdot \hat{\mathbf{u}}_i + \mathbf{r} \cdot \hat{\mathbf{u}}_j)^2}{1 + X(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j)} + \frac{(\mathbf{r} \cdot \hat{\mathbf{u}}_i - \mathbf{r} \cdot \hat{\mathbf{u}}_j)^2}{1 - X(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j)} \right\}, \tag{2.42}$$

$$\text{such that, } g(\chi) = 1 - \frac{\chi}{2r_{ij}^2} \left\{ \frac{(\mathbf{r} \cdot \hat{\mathbf{u}}_i + \mathbf{r} \cdot \hat{\mathbf{u}}_j)^2}{1 + \chi(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j)} + \frac{(\mathbf{r} \cdot \hat{\mathbf{u}}_i - \mathbf{r} \cdot \hat{\mathbf{u}}_j)^2}{1 - \chi(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j)} \right\}, \tag{2.43}$$

$$\text{and } g(\chi') = 1 - \frac{\chi'}{2r_{ij}^2} \left\{ \frac{(\mathbf{r} \cdot \hat{\mathbf{u}}_i + \mathbf{r} \cdot \hat{\mathbf{u}}_j)^2}{1 + \chi'(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j)} + \frac{(\mathbf{r} \cdot \hat{\mathbf{u}}_i - \mathbf{r} \cdot \hat{\mathbf{u}}_j)^2}{1 - \chi'(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j)} \right\}. \quad (2.44)$$

Now Eqs. (2.23) and (2.26) can be written as,

$$\sigma(\hat{\mathbf{r}}, \hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j) = \sigma_0 g(\chi)^{-1/2}, \text{ and } \epsilon_2(\hat{\mathbf{r}}, \hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j) = g(\chi'). \quad (2.45)$$

To find the derivatives of Eqs. (2.45) with respect to r (or r_{ij}) and $\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}$, we have to find the respective derivatives of $g(\chi)$ and $g(\chi')$. Using Eq. (2.42), the derivative of $g(X)$ with respect to r (or r_{ij}) is,

$$\begin{aligned} \frac{\partial g(X)}{\partial r} = & -\frac{X}{r_{ij}^2} \left[\frac{(\mathbf{r} \cdot \hat{\mathbf{u}}_i + \mathbf{r} \cdot \hat{\mathbf{u}}_j)}{1 + X(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j)} \left\{ \frac{\partial(\mathbf{r} \cdot \hat{\mathbf{u}}_i)}{\partial r} + \frac{\partial(\mathbf{r} \cdot \hat{\mathbf{u}}_j)}{\partial r} \right\} + \frac{(\mathbf{r} \cdot \hat{\mathbf{u}}_i - \mathbf{r} \cdot \hat{\mathbf{u}}_j)}{1 - X(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j)} \right. \\ & \left. \left\{ \frac{\partial(\mathbf{r} \cdot \hat{\mathbf{u}}_i)}{\partial r} - \frac{\partial(\mathbf{r} \cdot \hat{\mathbf{u}}_j)}{\partial r} \right\} \right] + \frac{X}{r_{ij}^3} \left\{ \frac{(\mathbf{r} \cdot \hat{\mathbf{u}}_i + \mathbf{r} \cdot \hat{\mathbf{u}}_j)^2}{1 + X(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j)} + \frac{(\mathbf{r} \cdot \hat{\mathbf{u}}_i - \mathbf{r} \cdot \hat{\mathbf{u}}_j)^2}{1 - X(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j)} \right\}, \end{aligned}$$

$$\text{where } \mathbf{r} \cdot \hat{\mathbf{u}}_i = r_{ij} \cos \theta_i, \text{ and } \frac{\partial(\mathbf{r} \cdot \hat{\mathbf{u}}_i)}{\partial r} = \cos \theta_i.$$

Here, θ_i is the angle between positional vector $\mathbf{r}$ and orientational unit vector $\hat{\mathbf{u}}_i$.

$$\begin{aligned} \frac{\partial g(\chi)}{\partial r} = & -\frac{\chi}{r_{ij}^2} \left[\frac{(\mathbf{r} \cdot \hat{\mathbf{u}}_i + \mathbf{r} \cdot \hat{\mathbf{u}}_j)}{1 + \chi(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j)} \{\cos \theta_i + \cos \theta_j\} + \frac{(\mathbf{r} \cdot \hat{\mathbf{u}}_i - \mathbf{r} \cdot \hat{\mathbf{u}}_j)}{1 - \chi(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j)} \{\cos \theta_i - \right. \\ & \left. \cos \theta_j\} \right] + \frac{\chi}{r_{ij}^3} \left\{ \frac{(\mathbf{r} \cdot \hat{\mathbf{u}}_i + \mathbf{r} \cdot \hat{\mathbf{u}}_j)^2}{1 + \chi(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j)} + \frac{(\mathbf{r} \cdot \hat{\mathbf{u}}_i - \mathbf{r} \cdot \hat{\mathbf{u}}_j)^2}{1 - \chi(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j)} \right\}, \quad (2.46) \end{aligned}$$

$$\begin{aligned} \frac{\partial g(\chi')}{\partial r} = & -\frac{\chi'}{r_{ij}^2} \left[\frac{(\mathbf{r} \cdot \hat{\mathbf{u}}_i + \mathbf{r} \cdot \hat{\mathbf{u}}_j)}{1 + \chi'(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j)} \{\cos \theta_i + \cos \theta_j\} + \frac{(\mathbf{r} \cdot \hat{\mathbf{u}}_i - \mathbf{r} \cdot \hat{\mathbf{u}}_j)}{1 - \chi'(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j)} \{\cos \theta_i - \right. \\ & \left. \cos \theta_j\} \right] + \frac{\chi'}{r_{ij}^3} \left\{ \frac{(\mathbf{r} \cdot \hat{\mathbf{u}}_i + \mathbf{r} \cdot \hat{\mathbf{u}}_j)^2}{1 + \chi'(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j)} + \frac{(\mathbf{r} \cdot \hat{\mathbf{u}}_i - \mathbf{r} \cdot \hat{\mathbf{u}}_j)^2}{1 - \chi'(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j)} \right\}. \quad (2.47) \end{aligned}$$

Using Eq. (2.41), the derivatives of $g(\chi)$ and $g(\chi')$ with respect to $\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_i$ and $\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_j$

SECTION 2.6: COMPUTATION OF THE INTERFACIAL PROPERTIES

are,

$$\begin{aligned}
\frac{\partial g(X)}{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_i)} &= -\frac{X}{2} \left[\frac{2(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_i + \hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_j)}{1 + X(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j)} \left\{ \frac{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_i)}{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_i)} + \frac{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_j)}{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_i)} \right\} + \right. \\
&\quad \left. \frac{2(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_i - \hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_j)}{1 - X(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j)} \left\{ \frac{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_i)}{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_i)} - \frac{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_j)}{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_i)} \right\} \right] \\
&= -X \left\{ \frac{(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_i + \hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_j)}{1 + X(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j)} (1 + 0) + \frac{(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_i - \hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_j)}{1 - X(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j)} (1 - 0) \right\}.
\end{aligned}$$

Therefore, $\frac{\partial g(\chi)}{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_i)} = -\chi \left\{ \frac{(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_i + \hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_j)}{1 + \chi(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j)} + \frac{(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_i - \hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_j)}{1 - \chi(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j)} \right\}$, and (2.48)

$$\frac{\partial g(\chi')}{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_i)} = -\chi' \left\{ \frac{(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_i + \hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_j)}{1 + \chi'(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j)} + \frac{(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_i - \hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_j)}{1 - \chi'(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j)} \right\}. \quad (2.49)$$

Similarly, $\frac{\partial g(X)}{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_j)} = -\frac{X}{2} \left[\frac{2(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_i + \hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_j)}{1 + X(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j)} \left\{ \frac{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_i)}{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_j)} + \frac{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_j)}{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_j)} \right\} + \right.$

$$\left. \frac{2(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_i - \hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_j)}{1 - X(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j)} \left\{ \frac{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_i)}{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_j)} - \frac{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_j)}{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_j)} \right\} \right]$$

$$= -X \left\{ \frac{(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_i + \hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_j)}{1 + X(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j)} (0 + 1) + \frac{(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_i - \hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_j)}{1 - X(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j)} (0 - 1) \right\},$$

Hence, $\frac{\partial g(\chi)}{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_j)} = -\chi \left\{ \frac{(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_i + \hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_j)}{1 + \chi(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j)} - \frac{(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_i - \hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_j)}{1 - \chi(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j)} \right\}$, (2.50)

$$\frac{\partial g(\chi')}{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_j)} = -\chi' \left\{ \frac{(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_i + \hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_j)}{1 + \chi'(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j)} - \frac{(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_i - \hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_j)}{1 - \chi'(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j)} \right\}. \quad (2.51)$$

Therefore, the derivatives of GB potential with respect to r , $\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_i$ and $\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_j$ are

$$\begin{aligned} \frac{\partial U}{\partial r} = & 4\epsilon_0\epsilon_1^\nu(\hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j) \left[\mu g^{\mu-1}(\chi') \frac{\partial g(\chi')}{\partial r} \left\{ \left(\frac{1}{R} \right)^{12} - \left(\frac{1}{R} \right)^6 \right\} + \right. \\ & \left. g^\mu(\chi')(6R^{-7} - 12R^{-13}) \frac{\partial R}{\partial r} \right], \end{aligned} \quad (2.52)$$

$$\begin{aligned} \frac{\partial U}{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_i)} = & 4\epsilon_0\epsilon_1^\nu(\hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j) \left[\mu g^{\mu-1}(\chi') \frac{\partial g(\chi')}{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_i)} \left\{ \left(\frac{1}{R} \right)^{12} - \left(\frac{1}{R} \right)^6 \right\} + \right. \\ & \left. g^\mu(\chi')(6R^{-7} - 12R^{-13}) \frac{\partial R}{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_i)} \right], \end{aligned} \quad (2.53)$$

$$\begin{aligned} \frac{\partial U}{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_j)} = & 4\epsilon_0\epsilon_1^\nu(\hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j) \left[\mu g^{\mu-1}(\chi') \frac{\partial g(\chi')}{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_j)} \left\{ \left(\frac{1}{R} \right)^{12} - \left(\frac{1}{R} \right)^6 \right\} + \right. \\ & \left. g^\mu(\chi')(6R^{-7} - 12R^{-13}) \frac{\partial R}{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_j)} \right]. \end{aligned} \quad (2.54)$$

The derivatives of R (Eq. (2.22)) with respect to r , $\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_i$ and $\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_j$ are,

$$\frac{\partial R}{\partial r} = \frac{1}{\sigma_0} \left\{ 1 + \frac{\sigma_0}{2} g^{-3/2}(\chi) \frac{\partial g(\chi)}{\partial r} \right\}, \quad (2.55)$$

SECTION 2.6: COMPUTATION OF THE INTERFACIAL PROPERTIES

$$\begin{aligned}
\frac{\partial R}{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_i)} &= \frac{1}{\sigma_0} \left\{ \frac{\partial r}{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_i)} - \frac{-\sigma_0}{2} g(\chi)^{-3/2} \frac{\partial g(\chi)}{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_i)} + \frac{\partial \sigma_0}{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_i)} \right\} \\
&= \frac{1}{\sigma_0} \left\{ 0 + \frac{\sigma_0}{2} g(\chi)^{-3/2} \frac{\partial g(\chi)}{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_i)} + 0 \right\} \\
&= \frac{1}{\sigma_0} \left\{ \frac{\sigma_0}{2} g(\chi)^{-3/2} \frac{\partial g(\chi)}{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_i)} \right\} = \frac{1}{2} g(\chi)^{-3/2} \frac{\partial g(\chi)}{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_i)}. \tag{2.56}
\end{aligned}$$

$$\text{Similarly, } \frac{\partial R}{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_j)} = \frac{1}{2} g(\chi)^{-3/2} \frac{\partial g(\chi)}{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_j)}. \tag{2.57}$$

Hence, using above equations, P_N^{IK} (Eq. (2.38)) and P_T^{IK} (Eq. (2.39)) can be calculated. Now, the pressure at a distance z due to left (LW) and right (RW) walls (Fig. 2.6) placed at z_{LW} and z_{RW} , respectively, are given by,

$$P_{LW}(z) = -\epsilon_W \sum_i \frac{\partial V_{WCA}}{\partial z_i} \Theta(z_i - z) \Theta(z - z_{LW}), \tag{2.58}$$

$$P_{RW}(z) = -\epsilon_W \sum_i \frac{\partial V_{WCA}}{\partial z_i} \Theta(z_{RW} - z) \Theta(z - z_i). \tag{2.59}$$

where z_i is the distance of i^{th} particle from the wall. Therefore, the normal and tangential pressure, including the pressure due to walls, are

$$P_N(z) = P_N^{IK}(z) + (P_{LW}(z) + P_{RW}(z))/A, \tag{2.60}$$

$$P_T(z) = P_T^{IK}(z). \tag{2.61}$$

In reduced units, the normal pressure tensor component is $P_N v_m / (k_B T)$, and the tangential pressure tensor component is $P_T v_m / (k_B T)$ [254], where $v_m = \pi \sigma_0^3 / 2$ is the volume of ellipsoidal molecule ($\sigma_{ee} = 3\sigma_0$, and $\sigma_{ss} = \sigma_0$). Using pressure tensor

relation, the wall-fluid interfacial tension γ is calculated as [214, 247, 250, 251]

$$\gamma = \frac{1}{2} \int_{z_{LW}}^{z_{RW}} (P_N(z) - P_T(z)) dz. \quad (2.62)$$

The interfacial tension in reduced units is $\gamma^* = \gamma v_m / (\eta_b \sigma_{ee} k_B T)$, where $\eta_b = v_m \rho$ is the bulk packing fraction [254]. In Eq. (2.62), the factor 2 in the denominator accounts for two interfaces: one near the left wall and the other near the right wall. In our case, $z_{LW} = 0$ and $z_{RW} = L_z$ (Fig. 2.6). Using the PT method, the surface tension has been calculated in various unconfined model systems, such as liquid-vapor interface in LJ fluid [241, 255], isotropic-nematic interface in hard and soft ellipsoids [96], vapor-isotropic [256] and vapor-nematic interface in GB fluid [256, 257]. It has also been successfully used for confined model systems such as polymeric thin films confined by two repulsive walls [247], hard spheres enclosed by WCA walls [214], and hard spherocylinders near hard walls [254]. Due to the successful implementation of the PT method in various model systems, we have also used this method to determine the interfacial tension in the confined GB system (study shown in Chapter 4).

Chapter 3

Interfacial stiffness of Gay-Berne nematic-smectic B interface

3.1 Introduction

During the nucleation and growth phenomena, a well-defined interface separates a nucleating phase from the surrounding mother phase, and the knowledge of the properties of such interfaces is crucial for better material processing. The nucleation phenomenon has been extensively studied in the systems of hard-spheres, one-component Asakura-Oosawa model (AO) [235], Ising model [258], colloid-polymer mixture [215, 259] and Lennard-Jones fluid [260]. However, in an LC material, it is expected that the shape anisotropy of liquid crystalline particles would result in a more intricate interfacial phenomenon. Now, the literature is full of exhaustive studies calculating the isotropic-nematic interface [87, 88, 95, 98]. However, much remains unknown about the nematic-smectic (nm-sm) interface. In this chapter, we have addressed and calculated the interfacial stiffness of the nematic-smecticB (nm-smB) interface. A nematic-smectic (nm-sm) interface can be observed by simulating an nm-sm phase coexistence, which is possible when the nm-sm phase transition is of the first order. However, the nature of the phase transitions between nematic and smectic (A, B, or C) phases is not clear yet; some literature argues for a continuous

phase transition [261, 262, 263] while others contest the same [264]. From computer simulations [186, 203, 206, 265, 266], theoretical [207, 267, 268, 269, 270] and experimental works [271, 272] only this much is clear so far that the type of phase transition between nematic and smectic phases depends on several factors, namely, the elongation or aspect ratio of the constituent particles, presence of particle inhomogeneity and external fields. However, for low aspect ratio mesogens, it is observed that the nm-smB phase transition remains first order, thus making the nm-smB coexistence region a possibility [186]. Here we have simulated LC mesogens with a low aspect ratio of $\kappa = 3$, and indeed, we could observe the nm-smB phase coexistence. Now, the interfacial properties, such as the interfacial tension or stiffness, can be calculated using various methods such as thermodynamic integration method [273], capillary wave theory [235], expanded ensemble simulation method [274], etc.. The interfacial properties depend upon several factors, such as the orientational symmetry between two coexisting phases, anchoring of particles near the interface, extent of shape anisotropy, temperature, and interaction between particles. [54, 86, 98, 109, 186]. All these factors result in characteristic fluctuations in the interface of a particular LC. For example, in an LC interface with normal anchoring, the interfacial fluctuations are more than in the interface with parallel anchoring [86], and there is zero fluctuation in an LC interface (i.e., a smooth LC interface) consisting of particles with infinite elongation [90]. Compared to the isotropic-nm interface, the nm-sm interface is expected to be comparatively smoother with lesser fluctuations owing to the two phases' higher orientational symmetry. Our simulation results show that the nm-smB interface is rough, fluctuating, and its position is not sharply defined. These observations made it possible for us to use the capillary wave theory (CWT) to determine the interfacial stiffness of the nm-smB interface [232, 235].

3.1.1 Simulation details

The simulations are performed in a cuboidal box filled with N numbers of GB ellipsoidal particles. The box is elongated along the z -direction such that the box lengths along x (L_x) and y (L_y) are the same (i.e. $L_x = L_y = L$) and length along z (L_z) is always greater than L . The GB ellipsoids have unit masses and their diameters along x , y , and z are in the ratio 1:1:3 (i.e., $\kappa = 3$). To obtain a system with nematic and smectic phases coexisting, the simulations are performed following a recipe consisting of three steps. In the first step, the simulation begins with a highly diluted low-density system (say $\rho_i = 0.01$) having N' particles distributed randomly over a large volume $V_i = N'/\rho_i$. The initial velocities and orientations of particles are chosen randomly. The system is then allowed to evolve under an isothermal-isobaric condition ($N'pT$ -ensemble) for 2.5×10^6 MD steps. The external pressure p is so set that the system evolves to a highly dense smectic-B phase. In the second step, the system is then allowed to equilibrate under an isochoric-isothermal condition ($N'VT$ -ensemble) for 2×10^6 MD steps. In the third step, the system is divided into two halves along the elongated z -direction. A fraction of particles (λ) is then deleted randomly from one half of the box to reduce its density compared to the other half and lower the overall density of the system. This new system, now having $N = \lambda N'$ number of particles, is then simulated again under the modified NVT -ensemble for 5×10^6 MD steps. At the end of the third step, the system's phase depends upon the value of λ we choose. If λ is too large, then we get an isotropic liquid state; on the other hand, if λ is too small, then the smectic phase survives throughout the system. But for some intermediate values of λ , we get systems where two phases coexist as shown in Fig. 3.1. This *three-step recipe* is then repeated for various system sizes with $L = 29.199, 33.333, 38.887, 43.064, 48.552, 62.445, 73.555, 80.563, 90.261$ and the number of particles, $N = 28360, 37269, 50718, 62214, 78986, 130679, 181334, 217172, 273212$, respectively, having $L_z \simeq 97$ for all. All the data reported here are for coexistence density, $\rho_{co} = 0.3450$, in which nearly half of the

system is in the nematic phase (represented by blue color) and the other half is in the smectic-B phase (represented by pink color) for all the system sizes taken. During a simulation, periodic boundary conditions are applied along all the directions, and the MD timestep size we used in our simulations is $\Delta t = 0.005$ units.

3.2 Results and discussion

3.2.1 Phase recognition

Using our *three-step recipe*, we have obtained the well-equilibrated systems with the nematic-smectic B phase coexistence. As periodic boundary conditions are applied during the simulations, two phases are separated by two interfaces along the z -direction. The snapshots on the left panels in Fig. 3.1 show the two coexisting phases. The left half of the system is in the nematic phase, having long-range orientational order but no positional order. The other half on the right is in the smectic-B phase, which has long-range orientational order and positional order owing to the layered arrangement of its constituent particles. The corresponding snapshots on the right side of Fig. 3.1 only show the smectic-B part. We have used the local bond order parameter, $Q_l(i)$ as introduced by Steinhardt *et al.* [275] to identify the particles that only belong to the highly ordered smectic-B phase and not to the fluid-like nematic phase. These parameters include the expansion of spherical harmonics, Y_{lm} and are defined by

$$Q_l(i) = \left(\frac{4\pi}{2l+1} \sum_{m=-l}^l |\bar{Q}_{lm}|^2 \right)^{1/2}, \quad (3.1)$$

$$\text{with } \bar{Q}_{lm}(i) = \frac{1}{Z_i} \sum_{j=1}^{Z_i} Y_{lm}(\theta(\mathbf{r}_{ij}), \phi(\mathbf{r}_{ij})), \quad (3.2)$$

where the separation between two neighboring particles i and j is given by the

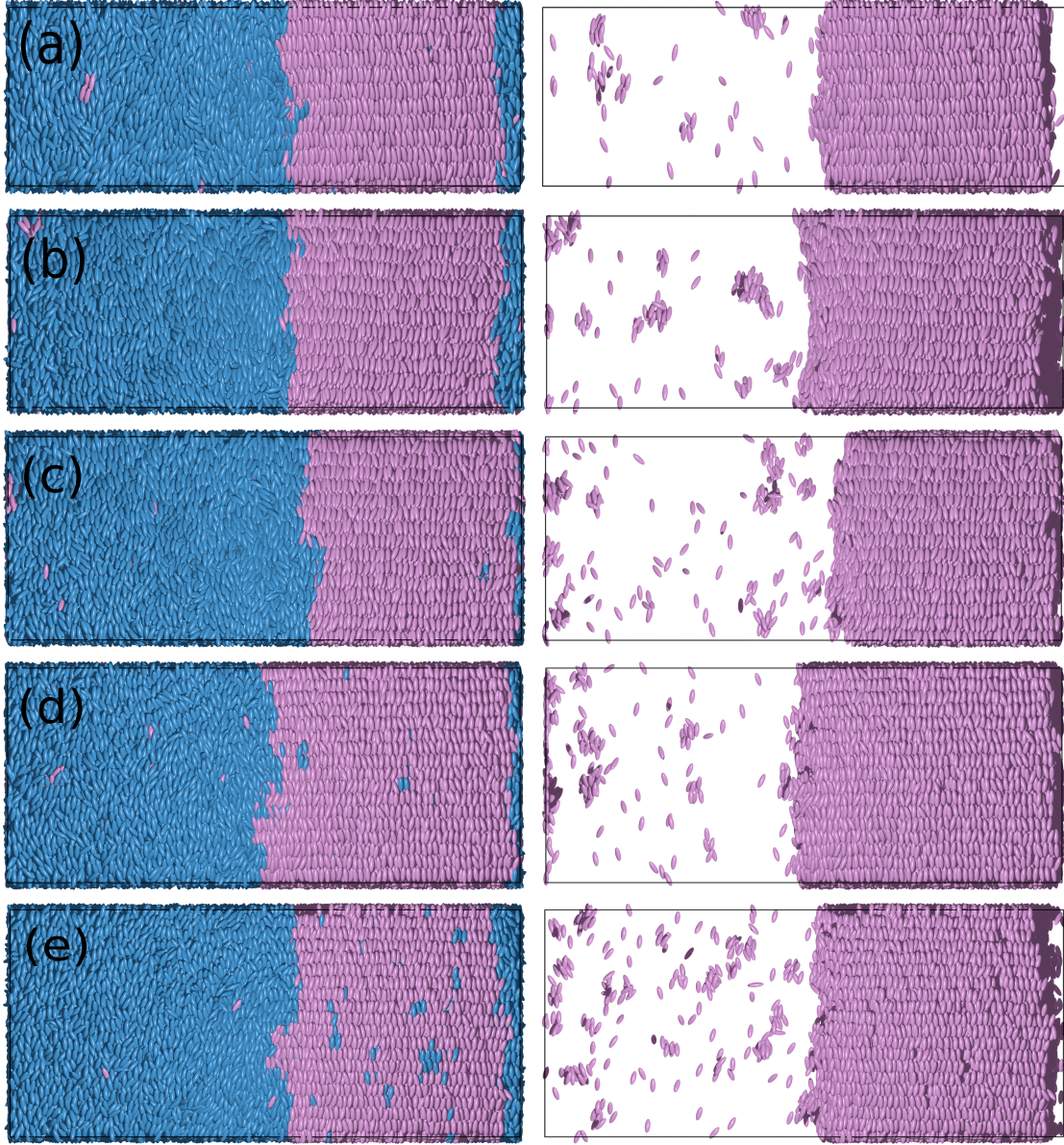


Figure 3.1: Left side snapshots show the coexistence of nematic (blue) and smectic-B (pink) phases; Right side snapshots show only the smectic-B phase. The particle identification is done by using local bond order parameters $q_6 q_6[z]$. The temperature and coexistence density are $T = 1.0$ and $\rho_{co} = 0.3450$, respectively. The system sizes are $L_x = L_y = 29$ (a), 33 (b), 38 (c), 43 (d), 48 (e) and $L_z \simeq 97$

distance vector $\mathbf{r}_{ij}$, the number of neighbors for any particle i within a given cut-off radius is given by Z_i and the polar bond angles between two neighbors i and j with respect to an arbitrary reference frame are $\theta(\mathbf{r}_{ij})$ and $\phi(\mathbf{r}_{ij})$. A modified version of order parameter of $Q_l(i)$ (Eq. 3.1) has been proposed by ten Wolde *et al.* as [276]

$$q_l q_l(i) = \frac{1}{Z_i} \sum_{j=1}^{Z_i} \sum_{m=-l}^l \tilde{q}_{lm}(i) \tilde{q}_{lm}(j)^*, \quad (3.3)$$

$$\text{with } \tilde{q}_{lm}(i) = \frac{\bar{Q}_{lm}(i)}{(\sum_{m=-l}^l |\bar{Q}_{lm}(i)|^2)^{1/2}} \quad (3.4)$$

We take $l = 6$ and find $q_6 q_6(i)$ for all particles in the system. To identify particles belonging to the smectic-B phase, we apply two criteria, the first one being $q_6 q_6(i) \geq 0.70$; $i = 1, N$, and the second one as $Z_i \geq 12$ [235]. The nearest neighbors count (Z_i) for each particle is calculated using the Voronoi construction for each configuration of the system. From the snapshots on the right panels of Fig. 3.1, we find that the nm-smB interface is rough and fluctuating. The properties of such an interface not only depend on the ordering of particles in the two phases but also on the relative angle between directors of the two phases [86, 107, 108, 109, 238]. The data presented here are for all cases when two directors are nearly parallel to each other and perpendicular to the interface normal. This is because, from energetic considerations, we believe that the parallel anchoring configuration (with the parallel smectic and nematic directors) will be comparably more stable than the other anchorings. In fact, we have observed the planar anchoring in significant fractions of our simulations. But, the precise determination of minimum energy anchoring remains to be explored. Therefore, we have consciously chosen to analyze the cases similar to the systems shown in Fig. 3.1 by running the simulations with different initial configurations. In Fig. 3.2, we have plotted the angular difference between nematic and smectic-B directors, $\mathbf{n}_{nm}(\theta_{nm}, \phi_{nm})$ and $\mathbf{n}_{sm}(\theta_{sm}, \phi_{sm})$, respectively, for

all the system sizes. It is clear that the two directors are nearly parallel to each other as the polar angular difference between them is close to zero. We believe that with the data from our q_6q_6 calculations, the interface between the two phases can be easily identified because the directors of the two phases are nearly parallel to each other and the interface (Fig. 3.2). However, we must add that if the directors of the two phases were not parallel to each other then the identification would have been trickier. Further, to check the stability of the nm-smB coexistence, the width

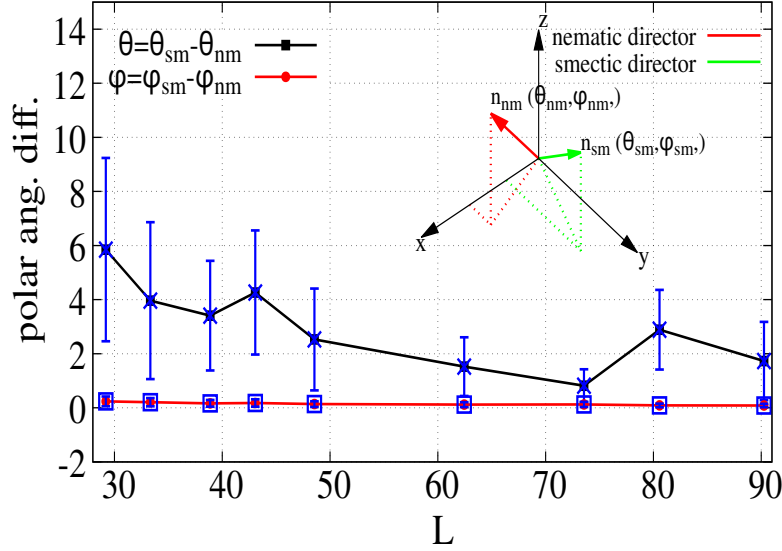


Figure 3.2: The relative angle between nematic and smectic directors in the nm-smB coexisting system for various system sizes. θ (circles) and ϕ (squares) represent the difference in the respective polar angles θ and ϕ of nematic ($\mathbf{n}_{nm}$) and smectic ($\mathbf{n}_{sm}$) directors as shown in the inset

of the nematic phase (Δw_{nm}) is measured and plotted with time, as shown in Fig. 3.3. The nematic width, on average, remains constant for 2×10^6 MD timesteps. However, the amplitude of fluctuations in the domain width or the phase breathing width decreases as the system size increases. This breathing width is related to the movement of the interface or change in the interfacial position. The dependence of fluctuating interfacial position on the system size is given by Schmitz *et al.* [277, 278, 279]. They showed that the interfacial position oscillates typically to the length scale that is proportional to the $\sqrt{L_z}/L$. To check this dependence in

our case, we have plotted the standard deviation in the averaged Δw_{nm} with the system size (L) and fitted it with the function $\sqrt{L_z}/L$ (shown in the inset of Fig. 3.3). Our plot also shows a similar dependence. The small amplitude and nearly periodic oscillations of the nematic width indicate the presence of a beautiful breathing phenomenon in the system. Such a breathing phenomenon, resulting from the thermally excited fluctuations occurring in an interface separating the two phases, forms capillary waves across the same.

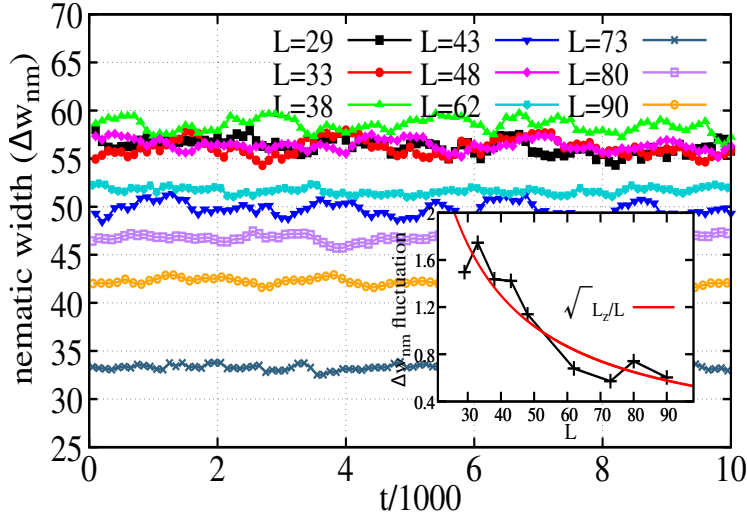


Figure 3.3: The variation of nematic width with time is shown here, indicating the breathing phenomenon wherein the width of two coexisting phases oscillates but remains stable with a fixed size on average. The data is at overall density $\rho_{co} = 0.345$ for all the system sizes. The inset shows the dependence of standard deviation in the mean Δw_{nm} on the system size as $\sqrt{L_z}/L$

3.2.2 Coexistence density range

The coexistence density (ρ_{co}) range for nematic and smectic-B phases is bounded between the freezing density (ρ_{nm}^f) of nematic phase into smectic-B phase and the melting density (ρ_{sm}^m) of smectic-B phase into the nematic phase, i.e. $\rho_{nm}^f < \rho_{co} < \rho_{sm}^m$. Here, the nm-smB coexisting density range (ρ_{co}) is determined using density profiles [86, 232, 257], which are shown in Fig. 3.4 for all the system sizes taken. To compute the density profile transverse to the interface, the system is sliced into

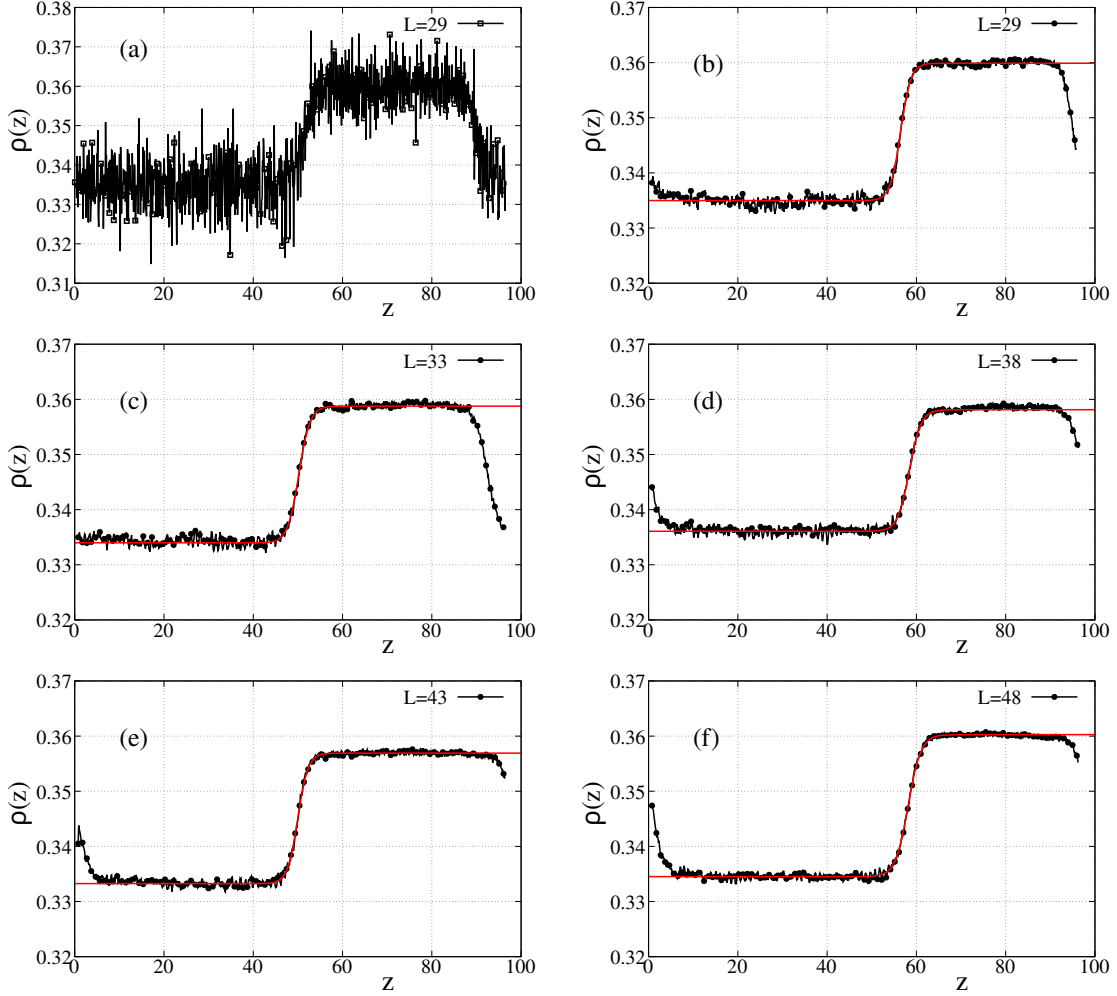


Figure 3.4: (a) Averaged density profile over 100 configurations of the system with $L = 29$ at temperature $T = 1.0$ and overall density, $\rho_{co} = 0.345$. (b)-(f) Running averaged density profiles over 100 configurations (black solid curve with filled circle) and hyperbolic tangent fit (red solid line) corresponding to various system sizes with $L = 29, 33, 38, 43, 48$ and $L_z \simeq 97$ at temperature $T = 1.0$ and overall system density, $\rho_{co} = 0.345$

several bins of thickness, Δz . The number of particles within each bin is then counted and normalized by the bin volume ($L^2 \Delta z$), giving the number density ($\rho(z)$) for a bin centered around z . The density profiles are averaged over a total of 10^4 configurations, which are taken one every 200 timestep in a sequence of 2×10^6 configurations of a well-equilibrated system. The nm-smB interface is located around the position z_0 , where the density change occurs. But a density profile averaged simply over all the 10^4 configurations can not give us the accurate location and

width of an interface, as due to the breathing phenomenon present in the system (Fig. 3.3), the interface would change its position with time. Thus, a blind averaging over all the 10^4 configurations would obscure the precise location and broaden the interfacial width. To circumvent this, we have performed averaging in the following way: the sequence of 10^4 configurations is sub-divided into a series of sub-sequences, each having only 100 configurations, and then the density profiles are obtained by averaging over each sub-sequence, i.e., only 100 configurations, as shown in Fig. 3.4(a). The interfacial position and width are obtained by fitting the density profile $\rho(z)$ to $f(z) = A + B \tanh((z - z_0)/w)$, where $A + B$ and $A - B$ are the bulk number densities of the two phases; z_0 and w are the position and width of the interface, respectively. To improve the estimation of the fitting parameters, first, we take a running average over the highly fluctuating density profiles and then fit $f(z)$ to the density profile, $\rho(z)$. The resultant running averaged density profiles and the corresponding fits are shown in Fig. 3.4 (b-f) for the first sub-sequence of 100 configurations. The process is repeated separately for all sub-sequences, and the corresponding fitting parameters (A, B, w, z_0) are calculated. Then, the bulk densities of two phases (ρ_{nm}^f and ρ_{sm}^m), the interfacial width (w) and position (z_0) are calculated by averaging over the corresponding fitting parameters obtained from fits of all sub-sequences. As two interfaces are present in the system due to periodic boundary conditions, the same steps are followed for both interfaces, and the averaging is done accordingly. The coexistence densities of nematic ($\rho_{nm}^f = A - B$) and smectic-B ($\rho_{sm}^m = A + B$) phases are listed in the Table 3.1. The system with overall density $\rho \leq \rho_{nm}^f$ will be in the pure nematic phase, and that with $\rho \geq \rho_{sm}^m$ will be in pure smectic-B phase. If $\rho_{nm}^f < \rho < \rho_{sm}^m$ (i.e., $\rho = \rho_{co}$), then the nm and smB phases can coexist. When the system's overall density is gradually increased from ρ_{nm}^f to ρ_{sm}^m , then the width of the nematic phase decreases progressively, and that of the smectic-B phase increases by following the simple lever rule of a binary mixture. The same has been verified by running several independent simulations at different

SECTION 3.2: RESULTS AND DISCUSSION

coexistence densities. We have also confirmed the coexistence range obtained by the density profile analysis by running independent simulations at overall density within and outside the coexistence range. It is to be noted here that the nm-smB

System Size	Nematic	Smectic-B
$L_x = L_y = L$	$\rho_{nm}^f \pm 0.002$	$\rho_{sm}^m \pm 0.002$
29	0.334	0.360
33	0.335	0.359
38	0.336	0.358
43	0.334	0.357
48	0.334	0.360

Table 3.1: The coexistence density range for nm and smB phases, found by density profiles, at $T = 1.0$ and $\rho_{co} = 0.345$ for different system sizes

coexistence density range at $T = 1.0$, as reported here, is slightly different from that reported by Miguel [36]. However, Miguel did not report the range exactly at $T = 1.0$ but did for $T = 0.95$ where $\rho_{nm}^f = 0.3449$ and $\rho_{sm}^m = 0.3596$. Looking at his data trend, we expect that at $T = 1.0$, Miguel's data would have been slightly higher than ours. As we have taken two orders of magnitude larger system that improves the statistical averages, we believe that the nm-smB coexistence range (as reported in Table 3.1) would improve over the earlier reported values.

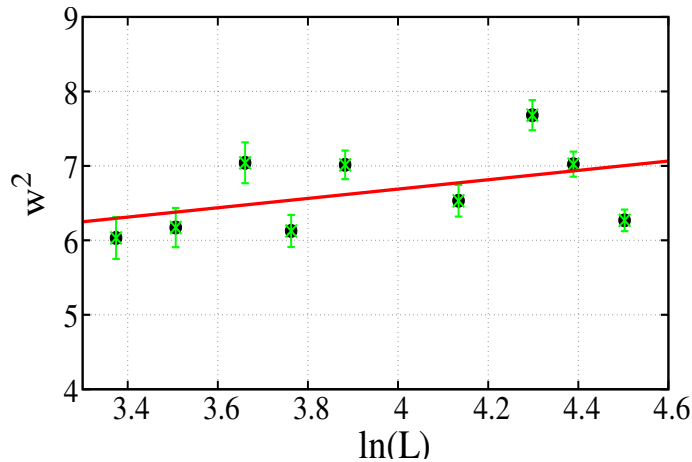


Figure 3.5: Mean squared interfacial widths are plotted versus the natural logarithm of the lateral size of the box for $L = 29, 33, 38, 43, 48, 62, 73, 80$, and 90 with standard deviation in the interfacial width

3.2.3 nm-smB interfacial energy

The nm-smB interfacial energy is computed by using CWT, according to which,

$$w^2 = w_0^2 + \frac{k_B T}{4\tilde{\gamma}} \ln(L) - \frac{k_B T}{4\tilde{\gamma}} \ln(l). \quad (3.5)$$

Therefore, CWT implies that the mean-squared width (w^2) increases linearly with $\ln(L)$ having the slope $\frac{k_B T}{4\tilde{\gamma}}$ (where $\tilde{\gamma}$ is the interfacial stiffness) and the intercept $w_0^2 - (k_B T/4\tilde{\gamma}) \ln(l)$. The elastic properties of nematic and smectic-B phases are non-trivial. However, we have still used Eq. (3.5) because we believe that so long as the directors of the two phases are nearly parallel, the interfacial properties can still be extracted as a first approximation. Therefore, to calculate the interfacial stiffness, firstly, the mean-squared interfacial widths (w^2), calculated from the density profiles, are plotted versus the corresponding $\ln(L)$, as shown in Fig. 3.5. The data is then fitted to a straight (solid red) line, giving us the slope (m). It is then used to calculate the interfacial stiffness as $\tilde{\gamma} = k_B T/4m$. In reduced units, $\tilde{\gamma}$ comes out to be $0.399k_B T/\sigma_{ee}^2 = 0.044/\sigma_{ss}^2$ (where σ_{ee} and σ_{ss} are the length and diameter of the GB ellipsoid).

3.3 Summary and conclusion

This chapter presents a molecular dynamics simulation study of the nm-smB phase coexistence in a thermotropic Gay-Berne liquid crystalline system. We found that computationally obtaining a well-equilibrated nm-smB phase coexistence in a finite volume is inefficient. Hence, we have developed a simple *three-step recipe* to obtain the coexistence in a fairly efficient manner. The coexistence range of the nematic and smectic-B phases at $T = 1.0$ is calculated by analyzing the density profiles along a direction transverse to the interface. By analyzing the coexisting phases' density profiles along a direction transverse to the interface, the coexistence range of the

SECTION 3.3: SUMMARY AND CONCLUSION

nematic and smectic-B phases at $T = 1.0$ is calculated. Then, using the local bond order parameter q_6q_6 , the particles belonging to the nematic and smectic-B phases are identified. Using this, we have been able to directly observe the existence of a rough interface separating the two phases (Fig. 3.1). Such a rough interface is expected as the aspect ratio of the GB particles used here is not large. Hence, using CWT analysis of the interface, the stiffness of the nm-smB interface is obtained that comes out to be $\tilde{\gamma}_{nm-smB} = 0.399k_BT/\sigma_{ee}^2 = 0.044/\sigma_{ss}^2$. It is important to note that such studies are an essential endeavor because accurate estimation of interfacial stiffness is indispensable for applications based on the crystal nucleation and growth phenomena.

Chapter 4

Interfacial tension between Gay-Berne isotropic fluid and wall

4.1 Introduction

The confined LCs have been extensively studied [280] using experiments [138, 134, 281], computer simulations [146, 282, 283] and various theoretical models [134, 284, 285] due to their several technological applications. In confined LCs, when an isotropic phase approaches the nematic or smectic phase, an ordered surface layer is developed with a finite or infinite limiting thickness, known as the orientational wetting phenomenon [286]. Therefore, the symmetry-breaking effect in confined LCs may result in positional and/or orientational alignment near the surface, which is transferred to the bulk via an anchoring mechanism [138, 282]. This mechanism of change in the bulk alignment according to the surface alignment is known as the anchoring transition. The anchoring transition can be achieved by changing the experimental conditions like temperature, conformation of the aligning agent, external electric field or surface interaction with fluid [282]. In literature, numerous studies are available for LC model systems confined by different surface potentials [282]. For example, the study of soft ellipsoids near hard rough walls [287, 288], hard ellipsoids [289, 290, 291, 292] and rods [293, 294] near hard walls, hard colloidal rods near

a soft wall [295], simple LC model near smooth wall [296], hard Gaussian overlap particles confined by slab geometry [280, 297], hard spherocylinders near parallel walls [298], hard planar walls [254, 299] and hard spherical cavity [300], and so on. Depending upon the nature of the surface, LCs may favor or restrain different molecular ordering [301]. For instance, free surfaces in free-standing films encourage the smectic (A or C) phase. In contrast, the surface in small pores promotes the nematic phase [301]. Further, depending upon the interaction potential between surface and LC molecules [282], homeotropic (perpendicular to the surface) [119, 284, 302, 303], planar (parallel to the surface) [282, 299], and tilted [280, 304] alignments have been observed. For instance, Allen *et al.* [291] observed the homeotropic surface anchoring of hard ellipsoids with a smooth, hard, repulsive wall. In contrast, the planar ordering was observed for hard spherocylinders near the hard wall [299]. Now, the widely used LC model is the Gay-Berne (GB) potential model. The GB molecules enclosed in slab geometry [194, 287, 305, 306, 307, 308, 309, 310], structured walls [311], spherical cavity [312], and cylindrical nanopores [313] have been well studied. The confinement of GB ellipsoids by parallel surfaces have resulted in tilted [305, 314], homeotropic [315] and planar anchoring states [306, 316, 317].

In this chapter, we present the study of determining the interfacial tension (γ_{WI}^*) required to form an interface between GB isotropic phase and soft, repulsive WCA wall. The GB parameters we have used here are (3, 5, 2, 1), which have been widely used in the studies of slab confined GB molecules [194, 305, 318, 319]. To the best of our knowledge, we believe that this is the first attempt to numerically calculate the value of γ_{WI}^* . The importance of this work arises in understanding the heterogeneous nucleation phenomenon when looked through the eye of Young’s equation [35].

4.1.1 Simulation details

The data presented here are collected from the canonical ensemble MD simulations using LAMMPS with timestep size, $\Delta t = 0.005$ units at temperature, $T = 1$ unit.

All the quantities are expressed in standard lj -units in LAMMPS. The simulations are carried out in a cuboidal box ($L_x \times L_y \times L_z$) filled with GB ellipsoids such that the lengths of the box in x and y directions are half of the length in the z -direction, i.e., $L_x = L_y = L \approx L_z/2$. Here, L_z is chosen to be greater than L to maintain a large separation between the walls so that walls do not interact with each other through the bulk fluid. Therefore, when L_z is large enough, we expect the bulk isotropic fluid to be similar to the corresponding fluid in the absence of confining walls [214]. The simulations are performed using a *three-step recipe*. In the first step, we take an isotropic box with periodic boundary conditions in all dimensions. The initial simulation begins with a highly diluted initial configuration having very low density (say $\rho = 0.01$) with randomly distributed $N = 16000$ particles in a large volume, $V = N/\rho$. The initial velocities and orientations of GB molecules are randomly chosen. This initial configuration is allowed to evolve for 2×10^6 MD steps under an isobaric-isothermal (NpT) condition. The external pressure (p) in the first step is so chosen to attain a highly dense final configuration in which the whole system acquires a nematic or smectic phase. After the NpT -ensemble, an equilibrated system is prepared in the second step by running the simulations under an isochoric-isothermal (NVT) condition for 2×10^6 MD steps. In the third step, the box is made non-periodic by placing two soft, smooth, repulsive WCA walls at the box's lower ($z = 0$) and upper ($z = L_z$) z -edges (Fig. 2.6). Note that before placing the walls, we increase L_z by $2 \times 2^{1/6}\sigma_W$ and delete particles within the distance of $2^{1/6}\sigma_W$ from lower and higher z -edges to avoid the system's instability. This confined system is allowed to evolve under NVT condition for 10^7 MD steps. A fraction of particles (mainly near the walls) is deleted from the simulation box to prepare system with low densities. The third step is repeated to achieve the confined isotropic bulk phase at different number densities. Following this, the data is collected after every 100 MD timesteps during a run of 10^6 MD timesteps, resulting in 10^3 well-equilibrated confined configurations. The above *three-step recipe* is also

used for a larger system size ($L \approx L_z/3$) to study the finite-size effects. Furthermore, the effect of varying WCA potential strength (ϵ_W) on the interface between the WCA wall and GB ellipsoids is also analyzed by using four different $\epsilon_W = 1, 4, 7$, and $10 \epsilon_0$ with $\sigma_W = \sigma_0$.

4.2 Results and discussion

4.2.1 MD simulation snapshots, pressure tensor profiles and nematic order parameter.

The GB particles confined by WCA walls are simulated at various number densities (ρ) at temperature $T = 1$ unit for two system sizes with $L \approx L_z/2$ and $L \approx L_z/3$. Due to the soft, repulsive walls, the particles are almost depleted from the regions that fall within the cut-off distance of $2^{1/6}\sigma_W$ from the walls. For system size $L = 27.9841$ and $L_z = 58.2131$ ($L \approx L_z/2$) (Fig. 4.1), the effect of the wall is found to be more prominent at higher densities than lower ones. For instance, the snapshot having the whole isotropic phase (Fig. 4.1(a)) at $\rho = 0.1000$ (bulk or central density, $\rho_b = 0.1034$) indicates the dewetting of the wall by GB ellipsoids. This implies that the wall does not significantly affect its nearby fluid at very low densities. But as density increases, the wall's influence strengthens, and particles start orienting normally to the wall surface (Fig. 4.3). The enhancing impact of wall with ρ is evident from the snapshots at densities $\rho = 0.2200$ ($\rho_b = 0.2230$) (Fig. 4.1(b)), $\rho = 0.2800$ ($\rho_b = 0.2793$) (Fig. 4.1(c)), $\rho = 0.3000$ ($\rho_b = 0.2979$) (Fig. 4.1(d)), and $\rho = 0.3090$ ($\rho_b = 0.3047$) (Fig. 4.1(e)). For densities $\rho = 0.2800$ and above, the smectic layering (having positional and orientational order) emerges in which the GB particles align homeotropically near the wall (i.e. particles' director is normal to the wall). When the bulk density approaches the isotropic-nematic phase transition density, the bulk particles start aligning in a particular direction.

SECTION 4.2: RESULTS AND DISCUSSION

The density $\rho = 0.3090$ ($\rho_b = 0.3047$) is very close to the isotropic-nematic phase transition density, as observed from the orientational order profile (Fig 4.7). It is

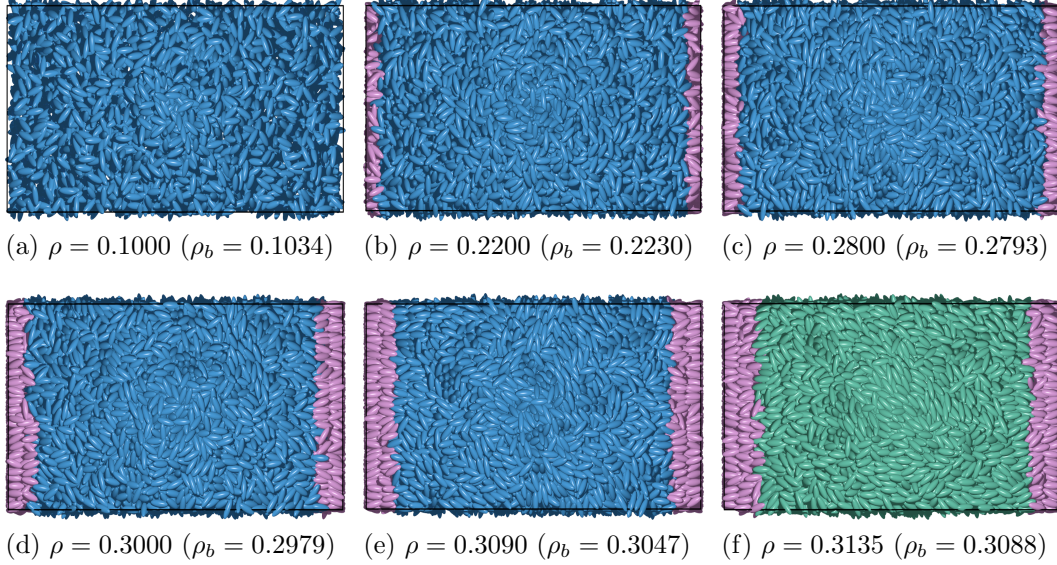


Figure 4.1: The snapshots (yz -view) of the system ($L = 27.9841$ and $L_z = 58.2131$) with walls are shown at various number densities. These images are made using POV-Ray and show the bulk isotropic phase (in blue color) with (a) no wall-induced order, (b) some order induced by the wall (shown by light pink color), (c), (d), (e) smectic layering near the wall; (f) the initiation of orientational order in bulk (shown by green color) with smectic layering near the wall. We have not used any order parameter to color the different phases. To visually distinguish between the smectic layering near the wall and the bulk phase, the particles lying within the distance of strong oscillations (layering) in the density profile are colored differently (done for visual clarity)

to be noted here that these snapshots (Figs. 4.1 and 4.4) are the side-views (or 2D-views) of the simulation box. In some images, the apparent appearance of the nematic alignment of particles at the center of the box is due to the limitation in presenting a 3D system using a 2D(or side)-view. In this planar view, some particles might appear to have the nematic alignment at the center, but overall or in a 3D sense, there is the isotropic phase at the center of the box, which is evident from the $Q_{zz}(z)$ data (Fig. 4.7). At the isotropic-nematic transition [36] density $\rho = 0.3135$ ($\rho_b = 0.3088$) (Fig. 4.1(f)), the particles near the smectic layers and in bulk, start attaining the orientational order. The present chapter mainly focuses

on the interface between the WCA wall and the bulk isotropic phase, i.e., up to $\rho = 0.3090$ ($\rho_b = 0.3047$).

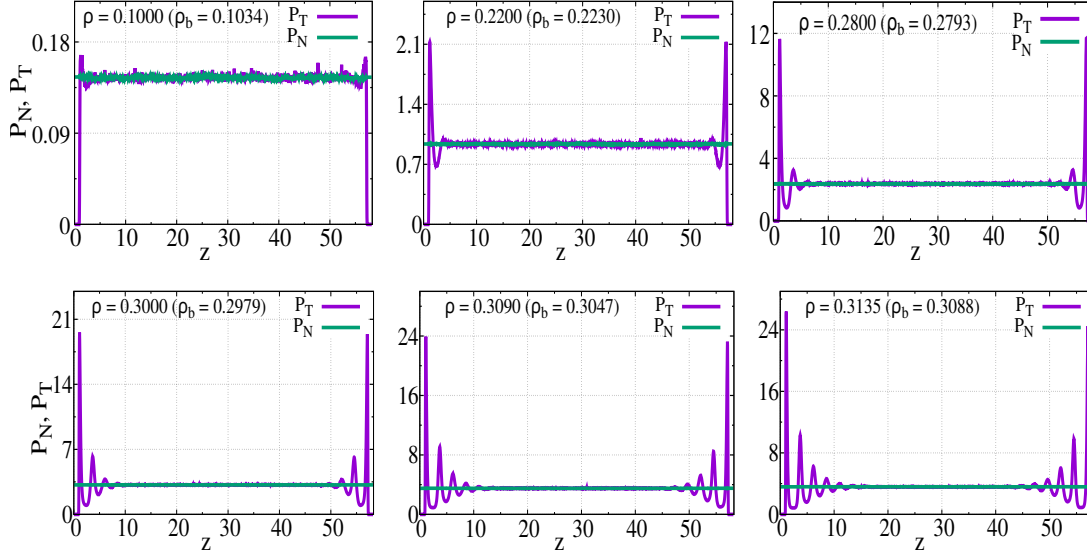


Figure 4.2: The reduced pressure tensor components (P_N and P_T) along z for $L = 27.9841$ and $L_z = 58.2131$ system size at various number densities

The similar effect of the wall upon increasing ρ can be seen in the profiles of pressure tensor components $P_N(z)$ and $P_T(z)$ (Fig. 4.2) and nematic (or orientational) order parameter near the wall (S_W) (Fig. 4.3). To calculate the pressure tensor profiles, the system is divided into bins of size equal to 0.03 units along the z -direction, and then the normal (P_N) and tangential (P_T) pressure (in reduced units) are calculated in each bin by averaging over 10^3 equilibrated configurations. As seen from the pressure tensor profiles (Fig. 4.2), the normal pressure component, P_N , remains constant irrespective of the distance from the wall, which is essential to maintain mechanical stability [247, 254]. The normal pressure coincides with the bulk tangential pressure and corresponds to the bulk scalar pressure. However, the tangential pressure component $P_T(z)$ depends upon the position z from the wall. The sharp peaks in $P_T(z)$ in the vicinity of the wall (Fig. 4.2) indicate the wetting of the wall by an ordered (orientational and/or positional) phase. These oscillations in $P_T(z)$ get stronger as the order near the wall increases upon increasing ρ .

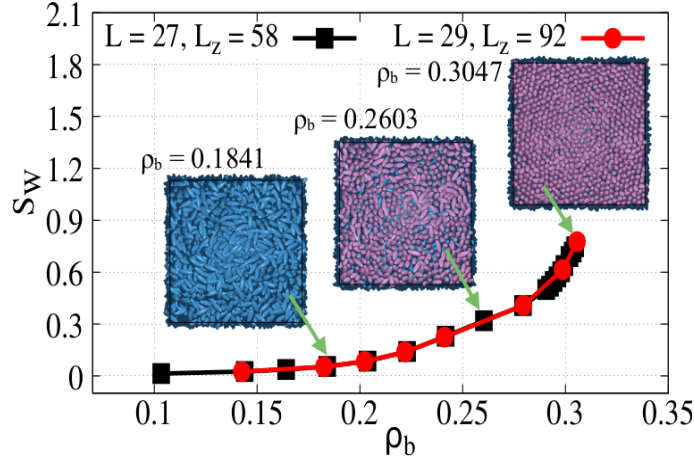


Figure 4.3: The variation in the nematic order parameter, calculated within the distance of $6\sigma_0$ (nearly two smectic layers) from both walls, is shown upon increasing bulk number density ρ_b for two system sizes. The snapshots shown here are the xy -view of GB particles near the left wall

Further, to numerically elucidate the wetting of the wall, the nematic (or orientational) order parameter, S_W , is calculated within the distance of $6\sigma_0$ (nearly two smectic layers) from both walls at all densities. The corresponding snapshots of GB particles near the left wall (xy -view) are shown for $\rho_b = 0.1841, 0.2603$, and 0.3047 (Fig. 4.3). As is apparent from Fig. 4.3, the orientational order in the vicinity of the wall increases with an increase in density. At low densities (see xy -view snapshot of $\rho_b = 0.1841$ in Fig. 4.3), S_W is nearly zero in the wall's domain due to the isotropic arrangement of particles near the wall. But as density increases, the particles' orientational order near the wall increases (as appears from the snapshot of $\rho_b = 0.2603$), and hence S_W increases. At higher densities, the particles near the wall acquire the positional and orientational order and, thus, arrange in smectic-like layers. A single smectic layer is observed at $\rho_b = 0.2793$ (Fig. 4.1(c)) where $S_W \approx 0.41$ (Table 4.1). Such a low value of S_W is because, in our calculations, we only included particles within a distance of nearly two smectic layers (rather than single) from the wall. With a further increase in ρ_b , the number of strong smectic layers increases. As is observed at $\rho_b = 0.3047$ (Fig. 4.1(e)), there is more than one smectic layer near the wall due to which S_W increases to around 0.75 (Table 4.1). The orientational order

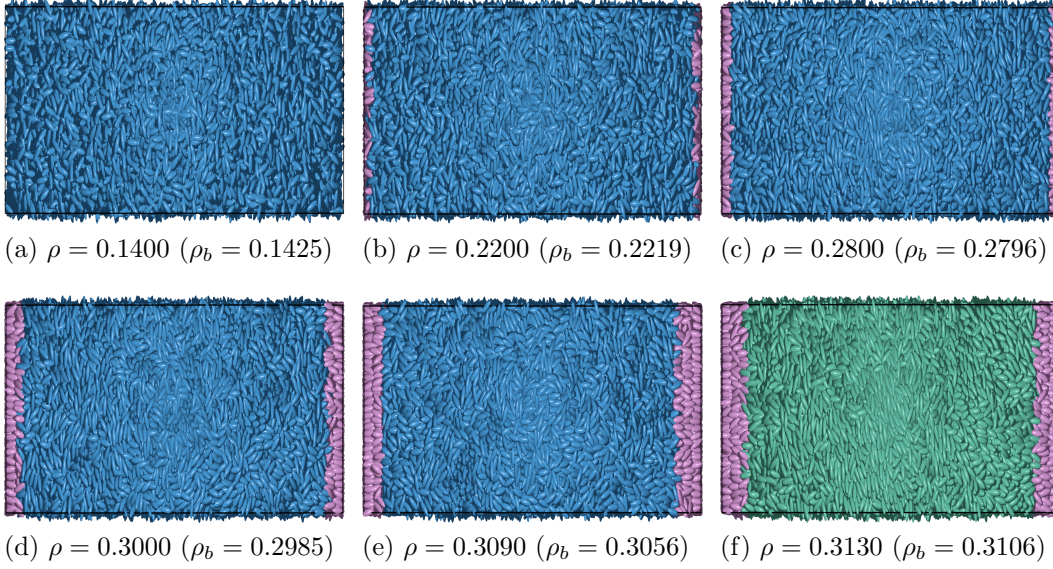


Figure 4.4: The snapshots (yz -view) of the system ($L = 29.4111$ and $L_z = 91.8788$) with walls are shown at various number densities. These images are made using POV-Ray and show the bulk isotropic phase (in blue color) with (a) no wall-induced order, (b) some order induced by the wall (shown by light pink color), (c), (d), (e) smectic layering near the wall; (f) the initiation of orientational order in bulk (shown by green color) with smectic layering near the wall

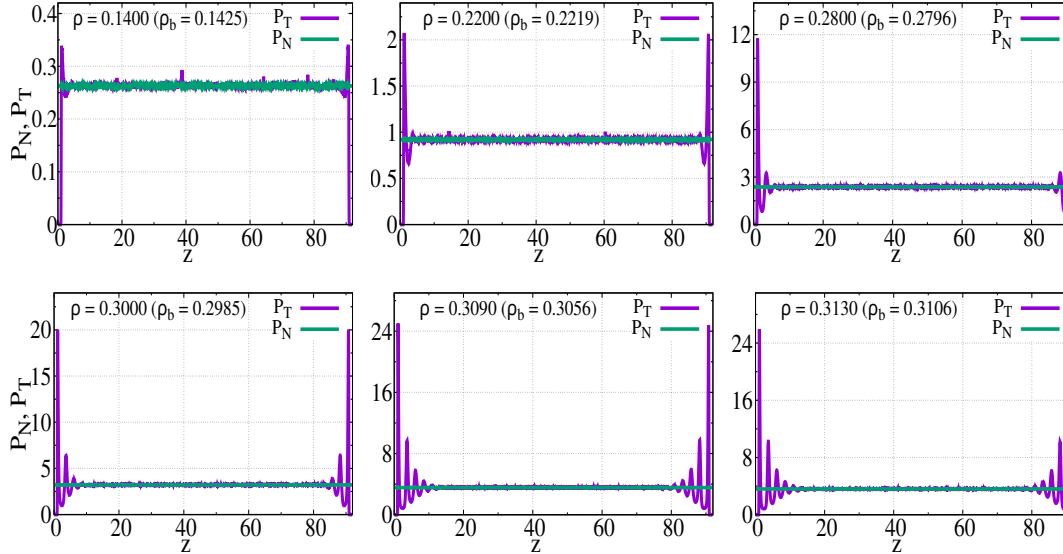


Figure 4.5: The reduced pressure tensor components (P_N and P_T) along z for $L = 29.4111$ and $L_z = 91.8788$ system size at various number densities

in bulk (S_b) is also calculated and given in Table 4.1. The very low values of S_b indicate that the bulk system is in the isotropic phase till $\rho_b = 0.3047$. However, at

the bulk isotropic-nematic transition density $\rho_b = 0.3088$, S_b comes out to be 0.315, indicating the presence of some orientational order in bulk.

Similar simulations and calculations are performed for a larger system size, i.e., $L = 29.4111$, and $L_z = 91.8788$ ($L \approx L_z/3$) to investigate the effects of system size on the confined GB ellipsoids. The snapshots, corresponding pressure tensor profiles, and the nematic order plot for larger system size are shown in Figs. 4.4, 4.5, and 4.3, respectively. These snapshots and plots show that this system behaves similarly to the smaller system size. Therefore, in our case, we can conclude that the smaller system size ($L = 27.9841 \approx L_z/2$) is enough to investigate the interfacial properties in the confined GB isotropic fluid system.

4.2.2 Density and local orientational order profiles

Anchoring plays a key role in determining the interfacial properties. Different types of anchoring (homeotropic/ planar/ tilted) result in different values of the interfacial tension (γ) or stiffness [98]. Therefore, before estimating γ , it is crucial to understand the type of anchoring of GB particles near the wall. The snapshots (Figs. 4.1 and 4.4) indicate that the bulk particles are oriented randomly, but the particles near the wall are oriented normally to the wall, i.e., homeotropic anchoring. In other words, the wall-normal is parallel to the director of the wall-induced ordered phase. Numerically, the wall-effectuated structural changes are observed using the number density $\rho(z)$ and orientational order $Q_{zz}(z)$ profiles. The orientational order profile along z (or normal to the walls) [282] is calculated as

$$Q_{zz}(z) = \frac{1}{N(z)} \sum_{i=1}^{N(z)} \left(\frac{3}{2} u_{i,z}^2 - \frac{1}{2} \right) \quad (4.1)$$

where $N(z)$ is the number of particles in the layer and $\mathbf{u}_i$ is the orientational vector of the i^{th} particle. The profiles $\rho(z)$ and $Q_{zz}(z)$ for smaller system size ($L = 27.9841$,

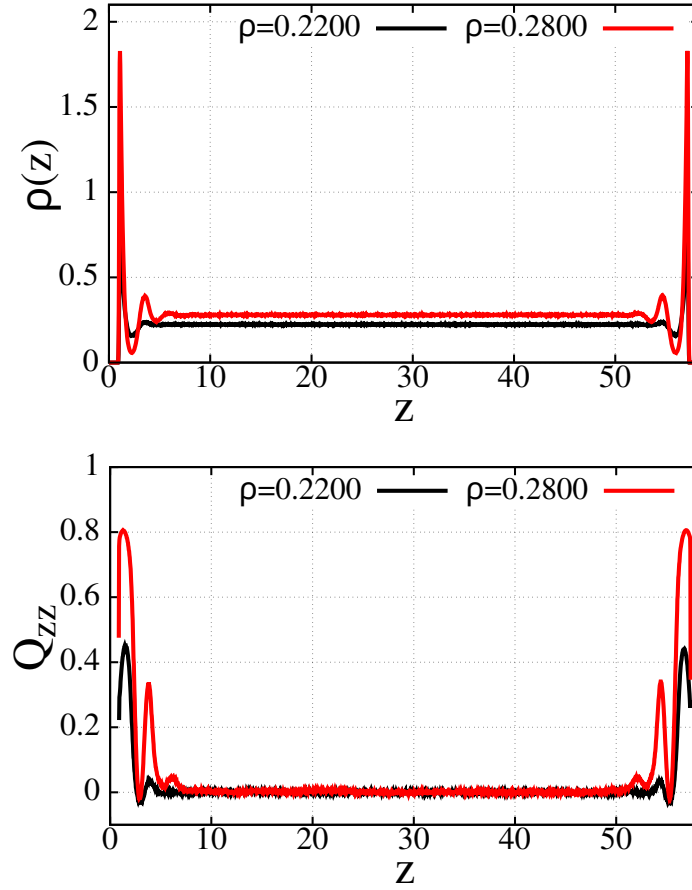


Figure 4.6: For $L = 27.9841$ and $L_z = 58.2131$ system size, the number density (top graph) and local orientational order (bottom graph) profiles at two overall densities exhibit the homeotropic alignment of GB particles near the wall

$L_z = 58.2131$) are plotted in Fig. 4.6 at two overall densities, $\rho = 0.2200$, and 0.2800 . $Q_{zz}(z)$ exhibit sharp peaks in high $\rho(z)$ regions, indicating the intrinsic coupling between number density and orientational order parameter. It confirms the homeotropic alignment [282] as peaks in $Q_{zz}(z)$ are closely correlated to $\rho(z)$ such that the maxima and minima in $\rho(z)$ correspond to the maxima and minima in $Q_{zz}(z)$, respectively. The local orientational order profiles $Q_{zz}(z)$ plotted at different ρ for both the system sizes (Fig. 4.7) provide the information about the onset of the orientational order in the bulk isotropic fluid as well as the direction of particles' orientations in bulk and near the wall. The value of $Q_{zz}(z)$ is zero as long as the phase is isotropic. As the particles in the bulk isotropic phase start

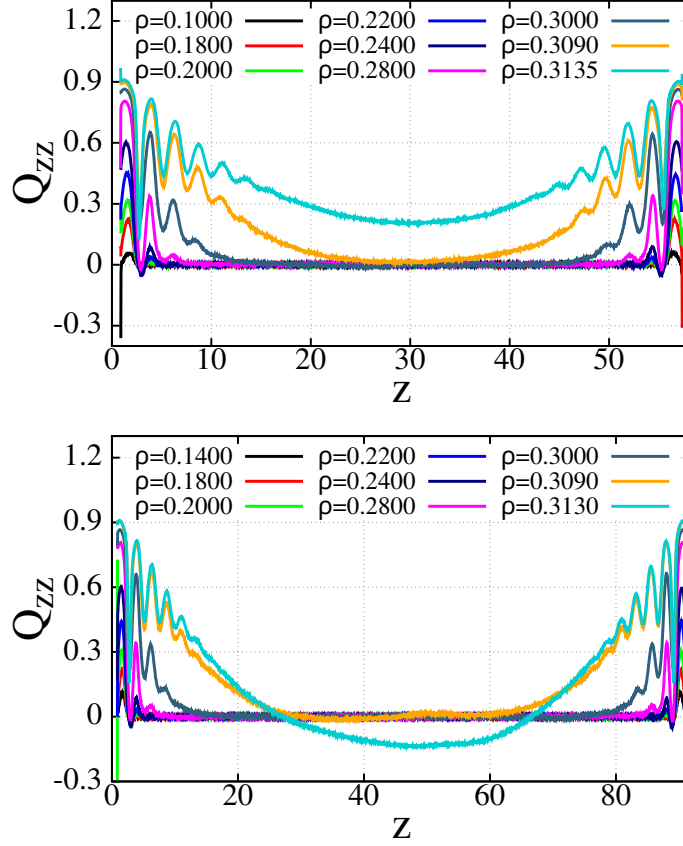


Figure 4.7: The local orientational order profiles $Q_{zz}(z)$ for system sizes, (a) $L = 27.9841$ and $L_z = 58.2131$, (b) $L = 29.4111$ and $L_z = 91.8788$, for various number densities with the bulk isotropic phase

orienting in a particular direction, $Q_{zz}(z)$ starts deviating from zero [309, 320, 321]. Now, depending upon the particles' orientations, i.e., they are along the wall-normal (z -direction) or not, $Q_{zz}(z)$ exhibits positive or negative values accordingly. For instance, if the fluid particles orient along the wall-normal, $Q_{zz}(z)$ exhibits positive values, but the deviation of particles' orientations from the wall-normal result in the negative values in $Q_{zz}(z)$. In our case, the positive value of $Q_{zz}(z)$ near the wall indicates that the particles are oriented normally to the wall [282]. However, at the isotropic-nematic phase transition density, Q_{zz} in bulk is positive for smaller system size and negative for the larger one. Therefore, for the system sizes and number densities we considered for the calculations, there is no system-size effect on the bulk isotropic phase. However, there is a considerable system-size effect on the GB

LC system at the isotropic-nematic transition density and above.

4.2.3 Interfacial tension

For this homeotropic alignment of particles near the wall, the wall-isotropic interfacial tension (γ_{WI}^*) is estimated using the pressure tensor method (Eq. (2.62)) for $\epsilon_W = \epsilon_0$ for both the system sizes. We have found that the variation of the interfacial tension (γ_{WI}^*) with bulk number density ρ_b is non-monotonic (Fig. 4.8) as was observed in the case of hard spherocylinders near hard walls [254]. For the smaller system size, γ_{WI}^* is very small at a very low density ($\rho_b = 0.1034$) due to the dewetting of walls by the bulk isotropic phase. As density increases, the confinement due to soft repulsive walls influences its nearby particles to start orienting along the wall-normal without much effect on the bulk disordered phase. Hence, the interfacial tension increases with density. The interfacial tension γ_{WI}^* attains a maximum value at $\rho_b = 0.2793$ corresponding to the onset of wall-wetting by a strong smectic layer (see yz -view snapshot 4.1(c) and xy -view snapshot for $\rho_b = 0.2793$ in Fig. 4.8). This wall-induced wetting transition further reduces γ_{WI}^* upon increasing ρ [254]. It is because, at densities above $\rho_b = 0.2793$, more particles near the initial smectic layer start orienting along the wall-normal due to the anchoring phenomenon [138]. As a result, a strong smectic layer reduces the energy required to wet the wall further, thus stimulating the wetting process. Similar behavior of varying interfacial tension with bulk number density is observed for another system size used.

Earlier studies reveal that the WCA wall-particle interaction strength can be used as a control parameter to modify the interfacial tension [214]. With a similar thought, we have analyzed the effect of varying WCA wall-GB interaction strength on WCA wall-isotropic interface by taking ϵ_W (in units of ϵ_0) = 1 (black), 4 (red), 7 (green), and 10 (blue) for smaller system size (Fig. 4.9). In our case, too, the varying wall-particle interaction strength impacts the interfacial tension (though not much at low densities). We have found that the variation of the interfacial tension

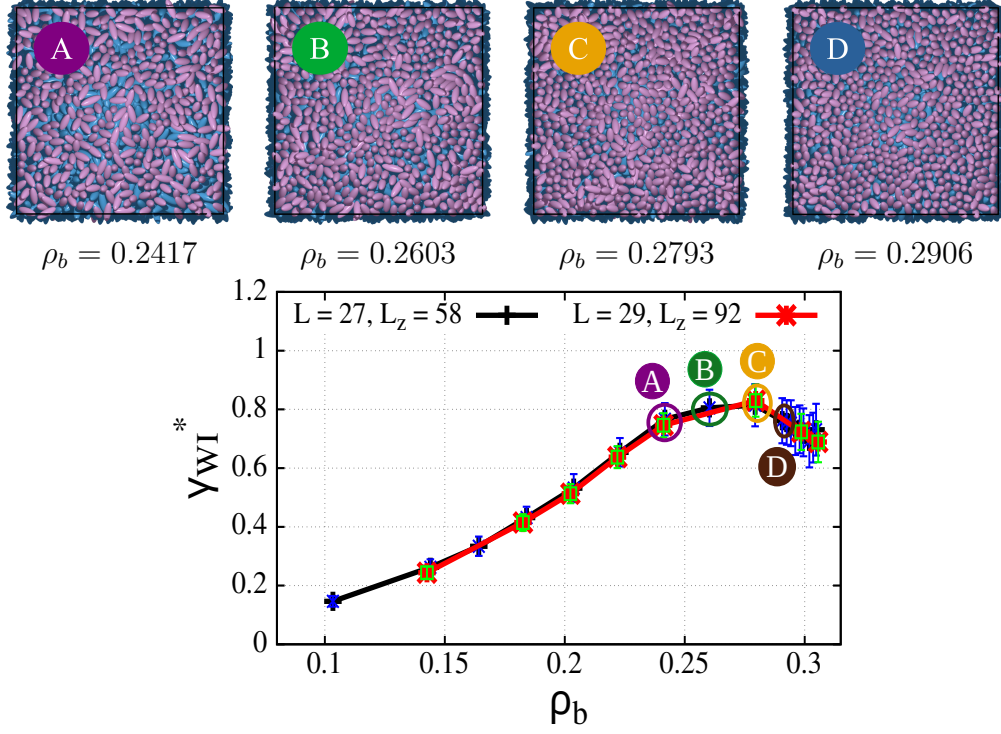


Figure 4.8: The variation of reduced interfacial tension (γ_{WI}^*) with bulk number density (ρ_b) is shown with error bars for two system sizes for $\epsilon_W = \epsilon_0$. The snapshots shown here are the xy -view of the smaller system size near the wall

with ϵ_W is similar to that of the WCA potential (as shown in the inset of Fig. 4.9). In other words, the higher the value of ϵ_W , the higher the γ_{WI}^* . γ_{WI}^* increases with ϵ_W because the average P_N and P_T increase but by a different amount. At very low densities with no wall-induced order near the wall, both P_N and P_T increase slightly, and hence γ_{WI}^* does not change notably with ϵ_W (Table 4.1). However, as ρ increases, the particles gain order near the walls, resulting in a significant rise in P_N , P_T and γ_{WI}^* with ϵ_W . From Fig. 4.9, we can see a regular trend in the variation of γ_{WI}^* with ϵ_W except at $\rho_b = 0.3047$ and $\epsilon_W = 10$. We believe that such an outlier data point for γ_{WI}^* at $\rho_b = 0.3047$ and $\epsilon_W = 10$ could be due to two reasons. Firstly, this density is very close to the isotropic-nematic phase transition density. Hence, it probably indicates the limitation of the pressure tensor method in calculating the interfacial tension at such a high density where the system is about to acquire the nematic order. Secondly, the strength of the wall potential

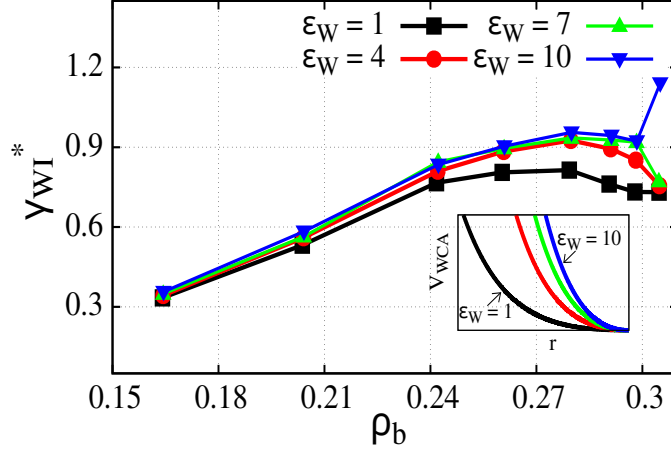


Figure 4.9: The reduced wall-isotropic interfacial tension (γ_{WI}^*) versus bulk number density (ρ_b) for four WCA wall strengths (ϵ_W in units of ϵ_0) is shown for $L = 27.9841$, and $L_z = 58.2131$ system size. The error bars are not shown here as they are similar to those shown in Fig. 4.8. The inset shows the behaviour of WCA potential for four potential strengths considered

($\epsilon_W = 10$) in this case might be too high for the stability of simulations at such a high density. The resultant data for the smaller system size is provided in Table 4.1. In literature, the surface and interfacial tension for different model systems have been calculated. However, despite the best of our efforts, we could not find any data of interfacial tension to compare with our data. So, we have compiled and presented the interfacial tension or stiffness values in Table 4.2 to depict the overall range of the values obtained so far and provide ready reference and completeness of the literature.

Table 4.1: Data obtained from MD-NVT simulations for the system size $L = 27.9841$ and $L_z = 58.2131$ having GB ellipsoids of aspect ratio $= \sigma_{ee}/\sigma_{ss} = 3$ confined between two smooth and soft repulsive WCA walls. Here, ϵ_W is the interaction strength between WCA walls and GB molecules, ρ is the overall number density of the system, ρ_b is the bulk number density, S_b is the orientational order in bulk, S_W is the orientational order within the distance of $6\sigma_0$ from each wall, P_N is the normal pressure tensor component, P_T is the transverse pressure tensor component, and γ_{WI}^* is the reduced interfacial tension of an interface between WCA wall and GB isotropic phase. All the quantities are in reduced units

ϵ_W	ρ	ρ_b	S_b	S_W	P_N	P_T	γ_{WI}^*
1	0.1000	0.1033	0.0006	0.0139	0.1448	0.1398	0.1463
1	0.1400	0.1440	0.0005	0.0257	0.2694	0.2604	0.2622
1	0.1600	0.1641	0.0003	0.0375	0.3663	0.3548	0.3339

SECTION 4.2: RESULTS AND DISCUSSION

1	0.1800	0.1841	0.0006	0.0550	0.4999	0.4851	0.4315
1	0.2000	0.2037	0.0004	0.0856	0.6842	0.6659	0.5319
1	0.2200	0.2230	0.0007	0.1412	0.9361	0.9137	0.6538
1	0.2400	0.2417	0.0014	0.2297	1.2738	1.2474	0.7663
1	0.2600	0.2603	0.0007	0.3190	1.7329	1.7053	0.8053
1	0.2800	0.2793	0.0024	0.4067	2.3657	2.3378	0.8142
1	0.2920	0.2906	0.0021	0.4998	2.8367	2.8105	0.7615
1	0.2940	0.2925	0.0024	0.5184	2.9216	2.8957	0.7555
1	0.2960	0.2943	0.0026	0.5459	3.0058	2.9799	0.7529
1	0.2980	0.2961	0.0014	0.5730	3.0907	3.0657	0.7264
1	0.3000	0.2979	0.0022	0.6021	3.1783	3.1531	0.7321
1	0.3020	0.2995	0.0056	0.6386	3.2590	3.2342	0.7219
1	0.3050	0.3019	0.0161	0.6902	3.3786	3.3548	0.6916
1	0.3070	0.3035	0.0254	0.7168	3.4548	3.4306	0.7038
1	0.3090	0.3047	0.0446	0.7472	3.5123	3.4872	0.7309
4	0.1600	0.1643	0.0007	0.0369	0.3675	0.3557	0.3427
4	0.2000	0.2041	0.0007	0.0883	0.6873	0.6681	0.5599
4	0.2400	0.2421	0.0006	0.2327	1.2814	1.2535	0.8101
4	0.2600	0.2607	0.0007	0.3244	1.7442	1.7138	0.8839
4	0.2800	0.2797	0.0024	0.4146	2.3816	2.3498	0.9256
4	0.2920	0.2910	0.0009	0.5061	2.8568	2.8260	0.8942
4	0.3000	0.2981	0.0031	0.6196	3.1947	3.1654	0.8516
4	0.3090	0.3048	0.0382	0.7619	3.5192	3.4932	0.7555
7	0.1600	0.1644	0.0001	0.0370	0.3678	0.3558	0.3487
7	0.2000	0.2042	0.0006	0.0886	0.6884	0.6690	0.5643
7	0.2400	0.2422	0.0007	0.2354	1.2841	1.2551	0.8450
7	0.2600	0.2609	0.0003	0.3253	1.7470	1.7163	0.8960
7	0.2800	0.2799	0.0009	0.4140	2.3863	2.3541	0.9353
7	0.2920	0.2912	0.0037	0.5059	2.8621	2.8303	0.9273
7	0.3000	0.2984	0.0010	0.6147	3.2038	3.1723	0.9192
7	0.3090	0.3047	0.0565	0.7648	3.5166	3.4901	0.7717
10	0.1600	0.1644	0.0002	0.0378	0.3682	0.3560	0.3565
10	0.2000	0.2042	0.0008	0.0884	0.6895	0.6695	0.5835
10	0.2400	0.2423	0.0013	0.2345	1.2846	1.2559	0.8347
10	0.2600	0.2610	0.0007	0.3239	1.7492	1.7181	0.9041
10	0.2800	0.2799	0.0002	0.4169	2.3886	2.3557	0.9560
10	0.2920	0.2913	0.0039	0.5072	2.8661	2.8337	0.9438
10	0.3000	0.2985	0.0067	0.6156	3.2083	3.1766	0.9228
10	0.3090	0.3051	0.0314	0.7640	3.5326	3.4934	1.1406

Table 4.2: The literature values of interfacial and surface tension for various model systems. Here, $\beta = 1/(k_B T)$, η and η_b are the overall and bulk packing fractions, v_m is the volume of a molecule, ρ' is the overlap density, γ_{WF} is the wall-fluid interfacial tension, γ_{WP} is the wall-polymer interfacial tension, c_I is the bulk isotropic-nematic transition density, c_b is the bulk density slightly below c_I and * indicates the reduced units. L and D are the molecular length and breadth, respectively

	Wall or solution	Model system	Interfacial or surface tension	Refs.
Confinement	Anisotropic corrugated surface, where L is half the period of corrugation	GB (σ is the interaction diameter of LJ particle)	$\gamma_x^* = 0.9, \gamma_y^* = 1.8$ for $L/\sigma = 1$	[322]
	Hard structureless walls	Hard spherocylinders	$\gamma_{WF}^* = \gamma_{WF} \beta v_m / (\eta_b \sigma_{ee}) = 0.3$ to 0.6 for $\eta_b = 0$ to 0.40	[254]
			$\gamma_{WI}^* = \beta \gamma_{WI} D^2 = 0.0590 \pm 0.0018$ for overall $\eta = 0.1020$	[323]
	Hard walls	Hard spheroplatelets (radius, a)	$\gamma_{WI} = \beta \gamma a^2 = 0$ to 0.05 for $\eta_b = 0$ to 0.48	[324]
		Hard rods	$\beta \gamma_{WI} L D = 0.05$ to 0.07 for $c_I - c_b = 10^{-8}$ to 10^{-2}	[294]
		Rodlike molecules (for $H/L = 3$ where H is separation b/w walls)	$\gamma_{WI}^* = \beta \gamma_{WI} D^2 = 0.02$ to 0.006 for $L/D = 10$ to 20	[325]
			$\gamma^* = 2.24$ to 2.36 for reduced chemical potential $\beta \mu = 7.6$ to 7.8	[326]
			$\gamma_{WP}/\gamma_W^{id} = 1$ to 6 (γ_W^{id} is for ideal polymer) for $\rho/\rho' = 0$ to 10	[327]
	Slitlike pore	Hard spherocylinders ($L/D = 3.7$)	$\gamma_{WI}^* = \beta \gamma_{WI} D^2 = -4.1036$	[328]

SECTION 4.3: SUMMARY AND CONCLUSION

	Solid walls	Hard rods (L/D = 10, 20)	$\gamma_{WF} = 0$ to $0.4 k_B T / LD$ for reduced bulk concentration = 0 to 1.0	[329]
	WCA	GB (3, 5, 2, 1)	$\gamma_{WI}^* = \gamma_{WI} v_m / (\eta_b \sigma_{ee} k_b T) = 0.1463$ to 0.7309 for $\rho_b^* = 0.1033$ to 0.3047	our present result
		Hard spheres	$\beta \gamma_{WF} \sigma^2 = 0.8$ to 2.5 for $\eta_b = 0.35$ to 0.5	[214]
		Asakura-Oosawa (colloid-polymer mixture)	$\beta \gamma_{WF} \sigma^2 = 1$ to 2 for $\eta_b = 0.4$ to 0.5	[215]
Immersed in solution	CTAB solution	Nematic 5CB	$\gamma_{WF} = 5.5$ to 7.5 for temperature = 27 to 41 °C	[330]
	Aqueous SDS solution	5CB	$\gamma = 10$ to 30 mN/m for SDS concentration = 0.01 to 6 mM	[331]
No confinement	Nematic-vapor interface for GB (3, 1, 2, 1)		$\gamma^* = \gamma \sigma_0^2 / \epsilon_0 = 0.369$ at $T^* = 0.59$	[257]
	Nematic-isotropic interface for soft rods (L/D = 10)		$\gamma_{IN} = 0.49 k_B T / L^2 = 0.0049 k_B T / D^2$ for $\beta \epsilon = 2$	[89]
	nCB LCs		surface tension = 29 to 36.5 dynes/cm for $T - T_{NI} = -20$ to 20 K	[332]

4.3 Summary and conclusion

In this chapter, the effects of confining WCA (Eq. (2.27)) walls on the GB (Eq. (2.22)) isotropic fluid are presented for a wide range of number densities. Using the simulation snapshots, pressure tensor profiles ($P_T(z)$), and the nematic order

parameter (S_W), the effect of the WCA walls on the GB LC system is observed. At low densities, the wall does not considerably affect the bulk isotropic phase. However, as density increases, the wall influences its nearby particles to acquire the positional and/or orientational order. Therefore, at high densities, the homeotropically aligned smectic layers are formed near the walls. The homeotropic alignment is verified by observing the snapshots, density profile ($\rho(z)$), and local orientational order profile ($Q_{zz}(z)$) (Figs. 4.1, 4.4, 4.6, and 4.7). As there is an ordered phase near the walls, the transverse pressure profile ($P_T(z)$) shows oscillations near the walls, which increase with ρ (Figs. 4.2, and 4.5). The order parameter S_W , calculated for a distance of nearly two smectic layers from the wall, is also found to increase continuously with bulk density ρ_b (Fig. 4.3).

The interfacial tension of an interface between the WCA wall and the GB isotropic phase (i.e., γ_{WI}^*) is calculated at various number densities using the pressure tensor method. The variation of γ_{WI}^* with ρ , is found to be non-uniform (Fig. 4.8). At low densities, there is a continuous increase in γ_{WI}^* with ρ until a strong smectic layer is formed near the wall at $\rho_b = 0.2793$. This smectic layer further instigates more particles to attain the orientational and/or positional order, resulting in more ordered layers at densities above $\rho_b = 0.2793$. Hence, a further increase in ρ induces wetting of the wall and thus reduces the interfacial tension. Two system sizes with $L \approx L_z/2$ and $L \approx L_z/3$ are simulated to analyze the finite-size effects. However, we have not observed any significant dependence of γ_{WI}^* on the system sizes we considered. In contrast, γ_{WI}^* is found to be dependent on wall-particle interaction strength (ϵ_W) (Fig. 4.9). It is found that the higher the ϵ_W , the higher the γ_{WI}^* . Such an increasing trend in γ_{WI}^* with ϵ_W continues except at $\rho_b = 0.3047$, which is close to the isotropic-nematic phase transition density. It might be due to increased agitation among the particles with an increase in ρ_b and ϵ_W , resulting in an irregular change in γ_{WI}^* . A thorough analysis of bulk behavior at higher densities, including the isotropic-nematic phase transition density, is still required. Understanding

SECTION 4.3: SUMMARY AND CONCLUSION

structural changes in LCs due to confinement is crucial for various technological purposes. We believe that calculating the WCA wall-GB isotropic interfacial tension is one crucial step toward understanding the heterogeneous nucleation and wetting phenomena in a liquid crystalline material.

Chapter 5

Droplet morphology in the nematic-smectic B phase coexistence

5.1 Introduction

The nucleation phenomenon in the case of spherical particles is widely studied using computer simulations [25, 276, 333] and theoretical calculations [13, 26, 334]. However, the nucleation phenomenon in materials composed of aspherical particles gives rise to more interesting interfacial properties. For a system containing rod-like particles, the droplet nucleation within various coexisting phases such as the isotropic-nematic [18], isotropic-smectic [74], isotropic-crystal [64] etc. has been widely studied. There are also various nucleation studies in mixtures containing liquid crystals [55, 335, 336]. In two-component systems, the nematic droplets in the form of tactoids, the formation of the smectic phase induced by the surface of metastable nematic droplets, and the smectic membranes in the form of twisted ribbons have been observed [336]. Experimental studies also revealed the generation of nematic ellipsoidal tactoids with rods aligned along the central axis of droplets [67, 68, 337]. The droplet elongation along the particles' director has also been observed in various

other studies [55,67,69]. In computer simulation studies, the Gay-Berne (GB) model is commonly used to simulate liquid crystalline particles. In most of the studies for constrained [141,312] and unconstrained [58] GB particles, the nematic droplets or tactoids have been observed. Due to the anisotropic GB potential, the tactoids can be stabilized due to the competing orientational and elastic effects [58], by changing the molecular elongation [338] and energy anisotropy parameter [339].

In this chapter, we present our study to investigate the possible shapes of nematic (nm) and smectic-B (smB) droplets formed during the nematic-smectic B (nm-smB) phase coexistence. The GB molecules with (3, 5, 2, 1) set of parameters are simulated at different nm-smB coexisting densities. To analyze the possible shapes of nm and smB droplets formed, an appropriate order parameter is needed to identify the nm and smB phases. In literature, the fluid phase has been distinguished from the solid phase by using two kinds of bond-order parameters [75]: (a) by calculating $\vec{q}_6 \cdot \vec{q}_6$ [340] such that for a particle, if six or more nearest neighbor bonds had $\vec{q}_6 \cdot \vec{q}_6 > 0.45$ then that particle was counted as a solid-like, (b) by counting the number of nearest neighbor bonds forming a straight line (i.e., pairs lying opposite to each other) for each particle such that the particles with five or more pairs of bonds forming an angle between 165° and 195° were considered as solid-like particles. A crystallinity criterion has been used in a system with rod-like particles to distinguish the crystalline phase from the isotropic liquid phase. This criterion states that if the surface-to-surface distance between two particles is less than $0.5D$ (D is the diameter of a rod-like particle) and the dot product of their orientation unit vectors is greater than 0.995, then these particles belong to the same crystallite [73]. In our recent work with GB (3, 5, 2, 1) potential (presented in Chapter 3), we investigated the planar nm-smB interface, and the phase identification was done by using local bond order parameter, q_6q_6 . There, we determined the nm-smB interfacial energy and coexisting density range [341]. Here, we show the possible morphology of equilibrated nm and smB droplets formed within the nm-smB phase

coexistence. Apart from the interest in pure statistical mechanical understanding of the nucleation phenomenon with nm and smB phases, the ability of liquid crystalline molecules to yield molecular assemblies is very appealing and has applications in various functional materials [342]. Even the small-sized LC droplets (nanodroplets) have biosensor applications [343].

5.2 Simulation details

The GB liquid crystalline system is simulated using the open-source LAMMPS package. All the simulations are performed using the canonical ensemble at temperature $T = 1$ unit with MD timestep size of $\Delta t = 0.005$. All the quantities are expressed in standard *lj*-units in LAMMPS. The simulations are carried out in a cubical box (i.e., $L = L_x = L_y = L_z$) with GB ellipsoids of unit masses and periodic boundary conditions in all directions. The diameters of GB ellipsoids along three body axes are $\sigma_x = \sigma_y = \sigma_0$ and $\sigma_z = 3\sigma_0$. To achieve the nm-smB phase coexistence, we have used a *three-step recipe* to simulate the GB LC system. The first of three steps is to get a well-equilibrated, dense smectic-B phase. To this end, the simulation begins with a highly diluted system (say, with initial density $\rho_0 = 0.01$), having N_0 number of particles within an initial large volume ($V_0 = N_0/\rho_0$). The initial positions, velocities, and orientations of these N_0 particles are randomly chosen. The system is then simulated for 2×10^6 MD timesteps under $N_0 p T$ -ensemble, i.e., isothermal-isobaric condition. The value of external pressure, p , is so chosen that the system evolves to a highly dense and ordered smB phase. The whole system is then simulated under an isochoric-isothermal condition, i.e., $N_0 V T$ -ensemble, for 2×10^6 MD timesteps to equilibrate the system and prepare for the next step of the simulation recipe. Thus, at the end of the first step, the simulation box is filled with an smB phase with density $\rho_1 > \rho_{co}$.

The second step is to obtain a system with coexisting nm and smB phases having overall density ρ within the coexistence range (i.e., ρ_{co}). For this, two different paths

are followed depending on whether ρ is closer to the lower (ρ_{nm}^f) or upper (ρ_{sm}^m) end of the nm-smB coexistence density range. Now, to have a system with ρ close to ρ_{nm}^f , some particles are randomly deleted from the simulation box barring a central cuboidal part of the box. However, for systems with ρ close to ρ_{sm}^m , the particles are deleted only from the central part of the simulation box (which was excluded for ρ close to ρ_{nm}^f). Note that the size of this central cuboid is nearly half of the system size. The number of particles to be deleted (N_d) is determined by the relation $N_d = V(\rho_1 - \rho)$ leaving $N = N_0 - N_d$ number of particles in the system. The new system is then simulated under a constant volume ensemble condition in two stages. In the first stage, only the box region from which the particles are deleted is allowed to evolve while keeping the remaining part frozen. Then, in the second stage, the whole system is simulated. In both stages, simulations are run each for 10^7 MD timesteps. In the third step, the data are collected after every 100 MD steps during the run of 10^4 MD timesteps. Therefore, all the calculations presented in this report are from these 100 equilibrated configurations.

Simulating the GB LC system is time-consuming, primarily owing to the complicated form of the GB potential (Eq. 2.22). The situation is compounded by the fact that capturing the true behavior of nucleation and the coexistence of phases is generally inhibited by the finite system size chosen for simulations. So, here is a glimpse of the time complexity of the simulations we performed. The LAMMPS package we used to perform the simulations has GPU acceleration enabled for the GB potential [344]. Our simulation recipe includes several steps (as discussed above). First is getting a well-equilibrated, highly dense phase (like a smectic-B phase). This step generally takes around 4 million MD steps and costs three days of simulation time. Next comes the step where the simulation is run for the longest time to get the coexisting phases. The time complexities of this step are presented in Table 5.1 to give a perspective of how time-consuming the simulations are.

Table 5.1: Time taken by simulations with different CPU cores and system sizes. The main component of the hardware used includes an Intel Xeon Silver 4114 CPU with a 2.20 GHz clock speed and an NVIDIA GeForce GTX 1080 Ti with a base clock speed of 1.481 GHz

System size, N	Number of timesteps	Cores used	Simulation time
60,492	2×10^7	8 CPU cores with GPU	4 days
60,834	2×10^7	12 CPU cores with GPU	2 days
3,21,375	2×10^7	12 CPU cores with GPU	10 days
3,16,783	2×10^7	16 CPU cores with GPU	14 days

5.3 Results and discussion

Using MD simulations, we have observed the possible shapes of nm and smB droplets formed within the nm-smB coexistence. For GB parameters (3, 5, 2, 1), the nm-smB coexisting density range is $0.334 \pm 0.002 < \rho_{co} < 0.360 \pm 0.002$ (as reported in Chapter 3), where the densities of pure nm and smB phases are $\rho_{nm}^f = 0.334 \pm 0.002$ and $\rho_{sm}^m = 0.360 \pm 0.002$, respectively [341]. Note that the droplets appear immediately as ρ exceeds ρ_{nm}^f in the thermodynamic limit but not in the case of the finite box [259, 345]. In the thermodynamic limit, the phase coexistence persists within the whole coexistence region, and the stability of the droplet is not affected by any boundary conditions. On the other hand, the droplet formation or dissolution is influenced by the boundary conditions in finite system size. Therefore, the coexistence density range might be shorter than in the thermodynamic limit. To understand such finite-size effects, we have run the simulations for two system sizes within the nm-smB coexisting density range. As these simulations are very time-consuming and require high computational power, we have simulated the systems with L equal to 55.4921 and 97.1956 for better analysis of the droplets formed.

5.3.1 Phase identification with a sub-box technique

After achieving the equilibrium configurations of the system with the nm-smB coexistence using our *three-step recipe*, the important task was to identify the two phases to locate the nm-smB interface. In our recent work [341] (presented in Chapter 3), we successfully identified the nm and smB phases separated by a planar interface using a particle-based microscopic order parameter, i.e., the local bond order parameter (q_6q_6). Hence, we expected q_6q_6 to be suitable for the present work, too. However, it turns out that q_6q_6 could only identify the nm-smB planar interface but not the non-planar interfaces formed between the nm and smB phases. Hence, we take an alternative route for the identification strategy based on the orientational order parameter. The orientational order parameter is given by $S = \langle (3 \cos^2 \theta - 1)/2 \rangle$, where θ is the angle between a particle's orientational vector and director. Now, this parameter is an averaged quantity of the particles' orientations. Here, we have calculated the orientational order in the local environment by dividing the simulation box into small regions called sub-boxes. We consider this method of calculating the orientational order in sub-boxes (S_{sb}) a local-averaging technique because we take the small sub-boxes for calculations instead of the whole simulation box. Thus, we have used a local-averaging phase identification technique to distinguish between nm and smB phases. For the sensible calculation of S_{sb} , the sub-box size needs to be chosen carefully. This is achieved by plotting the orientational order distributions for different sub-boxing scales and we looked for a well-behaved S_{sb} distribution. Hence, after several trials, the sub-box scaling is chosen to be around 5 because it results in well-behaved orientational order distributions (as shown in Figs. 5.1, and 5.2, respectively). Apart from the locally averaged orientational order distributions, we also calculated the number density in sub-boxes (ρ_{sb}) and plotted the corresponding distributions as shown in Fig. 5.3 for larger system size. The ρ_{sb} distributions also evince the nm-smB coexistence, but they are not well-behaved and thus are not good enough to identify the shapes of nm and smB droplets formed. Therefore, in

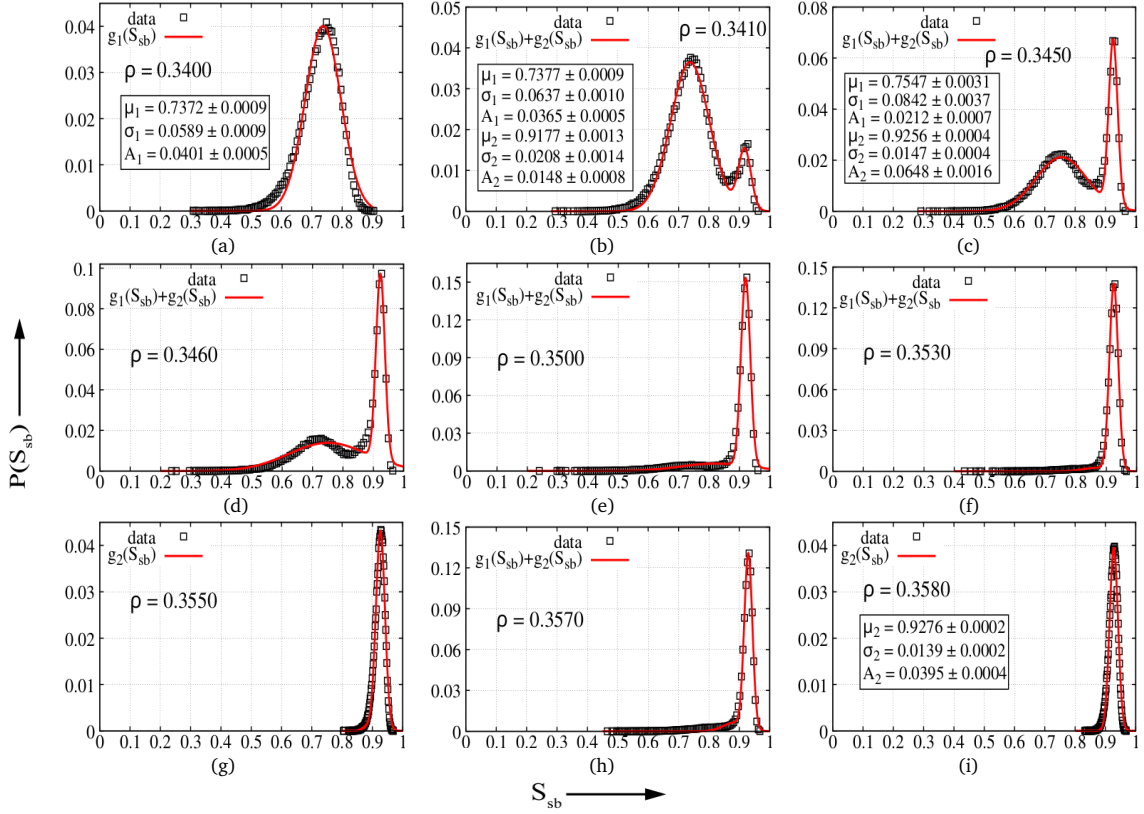


Figure 5.1: The plots of the orientational order distributions at different number densities for smaller system size, i.e., $L = 55.4921$. The orientational order (S_{sb}), plotted along the horizontal axis, is calculated using the sub-box technique. The symbols (black squares) indicate the data points, and the line (red-colored) represents the fitted Gaussians; $g_1(S_{sb})$ is the Gaussian distribution for the nematic peak and $g_2(S_{sb})$ for the smectic peak. The errors in μ , σ , and A for the nematic and smectic Gaussian fitting curves are also given at some densities

our present work, we have used the S_{sb} distributions to identify the nm and smB phases during the nm-smB coexistence. To accomplish this, the simulation box is divided into $11 \times 11 \times 11$ sub-boxes of dimensions $5.0447 \times 5.0447 \times 5.0447$ in x , y and z directions for smaller system size and $19 \times 19 \times 19$ sub-boxes of dimensions $5.1156 \times 5.1156 \times 5.1156$ in x , y and z directions for larger system size. Then, the orientational order is calculated in each sub-box and averaged over 100 equilibrated configurations. The S_{sb} distributions are plotted as shown in Figs. 5.1 and 5.2 for smaller ($L = 55.4921$) and larger ($L = 97.1956$) system sizes, respectively and fitted with the unimodal or bimodal Gaussians of the form $A \exp(-(x - \mu)^2/2\sigma^2)$. The

double peaks in these distributions indicate the coexistence of two phases, viz., nm and smB phases. However, when a single nm (Figs. 5.1(a) and 5.2(a)) or smB (Figs. 5.1(i) and 5.2(i)) phase is formed without any coexistence then these distributions show only one peak at around $S_{sb} \approx 0.75$ for nm and $S_{sb} \approx 0.92$ for smB phase. Therefore, during coexistence, we could safely assume that the sub-boxes with S_{sb} values less than 0.8 contain the nm-like particles, and those with S_{sb} values greater than 0.9 contain the smB-like particles.

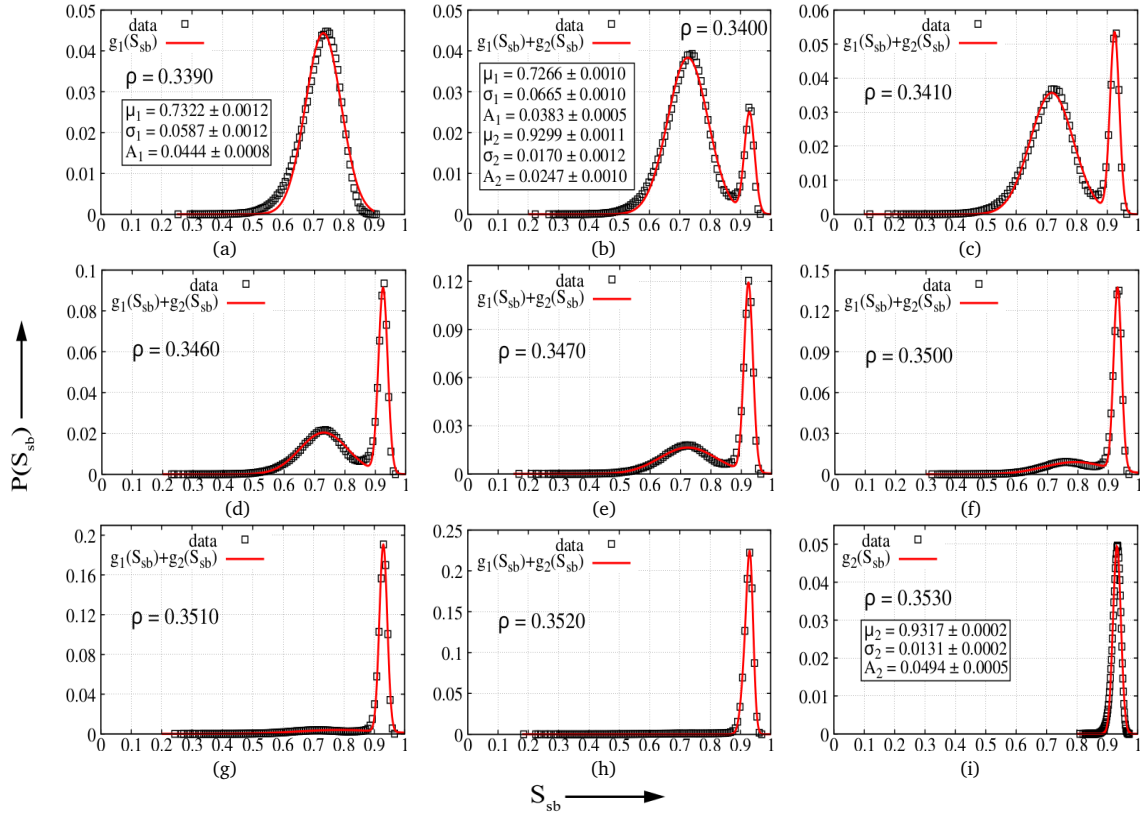


Figure 5.2: The plots of the orientational order distributions at different number densities for larger system size, i.e., $L = 97.1956$. The orientational order (S_{sb}) plotted along the horizontal axis is calculated using the sub-box technique. The symbols (black squares) indicate the data points, and the line (red-colored) represents the Gaussian fitting curve; $g_1(S_{sb})$ is the Gaussian distribution for the nematic peak and $g_2(S_{sb})$ for the smectic peak. The errors in μ , σ , and A for the nematic and smectic Gaussian fitting curves are also given at some densities

The snapshots shown in Figs. 5.4, 5.6, 5.7, and 5.8 are generated by using a criterion of identifying the sub-boxes with $S_{sb} < 0.8$ to have the nematic-like and

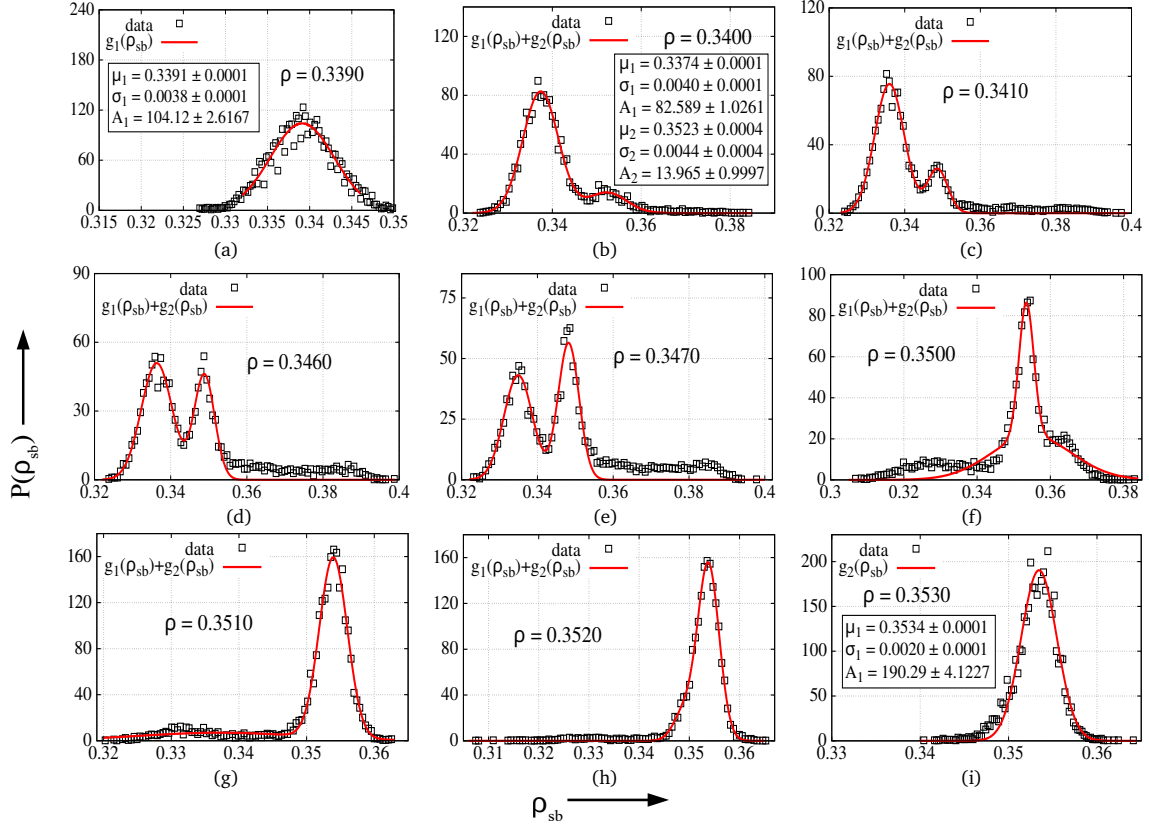


Figure 5.3: The plots of number density distributions at different number densities for larger system size, i.e., $L = 97.1956$. The number density (ρ_{sb}), plotted along the horizontal axis, is calculated using the sub-box technique. The symbols (black squares) indicate the data points, and the line (red-colored) represents the Gaussian fitting curve; $g_1(S_{sb})$ is the Gaussian distribution for the nematic peak and $g_2(S_{sb})$ for the smectic peak. The errors in μ , σ , and A for the nematic and smectic Gaussian fitting curves are also given at some densities

$S_{sb} \geq 0.9$ to have the smectic-like phase. The images in the top row of Figs. 5.4, 5.6, 5.7, and 5.8 represent the whole system, i.e., the nematic phase, smectic phase, and interface. However, the images in the second and third rows of Figs. 5.4, 5.6, 5.7, and 5.8, represent the single phase with only nematic droplet (i.e., only sub-boxes having $S_{sb} < 0.8$) or the smectic droplet (i.e., only sub-boxes having $S_{sb} \geq 0.9$) at different viewing angles. In the third row, the planar view (i.e., xy or yz , or xz) of the droplet is shown for a better view of the droplet's phase. In these images, the particles in the nm-like and smB-like sub-boxes are colored in blue and pink, respectively. Meanwhile, the green-colored boxes in the top rows

of Figs. 5.4, 5.6, 5.7, and 5.8 are the sub-boxes having the intermediate values of S_{sb} (i.e., $0.8 \leq S_{sb} < 0.9$), representing the nm-smB interface. This local-averaging method is unsuitable to see any microscopic droplet (say, consisting of only a few GB molecules). Although this criterion gives us a rough image of an interface, it still gives an impression of the droplet shape formed in the simulations. To conclude, such a criterion of using the sub-box orientational order parameter is useful to differentiate between the coexisting nm and smB phases separated by planar and non-planar interfaces.

5.3.2 Shapes of nm and smB droplets

To investigate the different possible shapes of nm and smB droplets formed within the nm-smB coexistence, we begin with the nematic density of $\rho_{nm}^f = 0.3340$, that is the lower end of the nm-smB coexistence density range [341]. For smaller system size (i.e., $L = 55.4921$), no smB droplet is observed for $\rho \leq 0.3400$ and the whole system is spanned by the nematic phase (Figs. 5.4(a), and 5.4(a')). However, as we have discussed earlier (at the start of sec. 5.3), it is expected that in the thermodynamic limit, smB droplet would form in a system with density just above $\rho_{nm}^f = 0.3340$. Here, we did not see any droplet up to density $\rho = 0.3400$, possibly due to the following two reasons. Firstly, due to the finite system size effects [259, 345] and secondly, the local-averaging method of calculating the orientational order in sub-boxes (S_{sb}) could not identify the small droplets formed for $0.3340 \leq \rho \leq 0.3400$. The green-colored sub-boxes (Fig. 5.4(a)), representing the nm-smB interface, might have microscopic-sized droplets that the sub-box identification technique could not identify. To illustrate this, we have shown three possible droplet scenarios (in Fig. 5.5) that might be difficult for our method to identify. In the first case, Fig. 5.5(a), the small-sized droplet may not be identified, as the sub-box also includes a large number of particles from the surrounding phase, hence the averaged order parameter S_{sb} within the sub-box may remain different from the droplet's phase. In the second

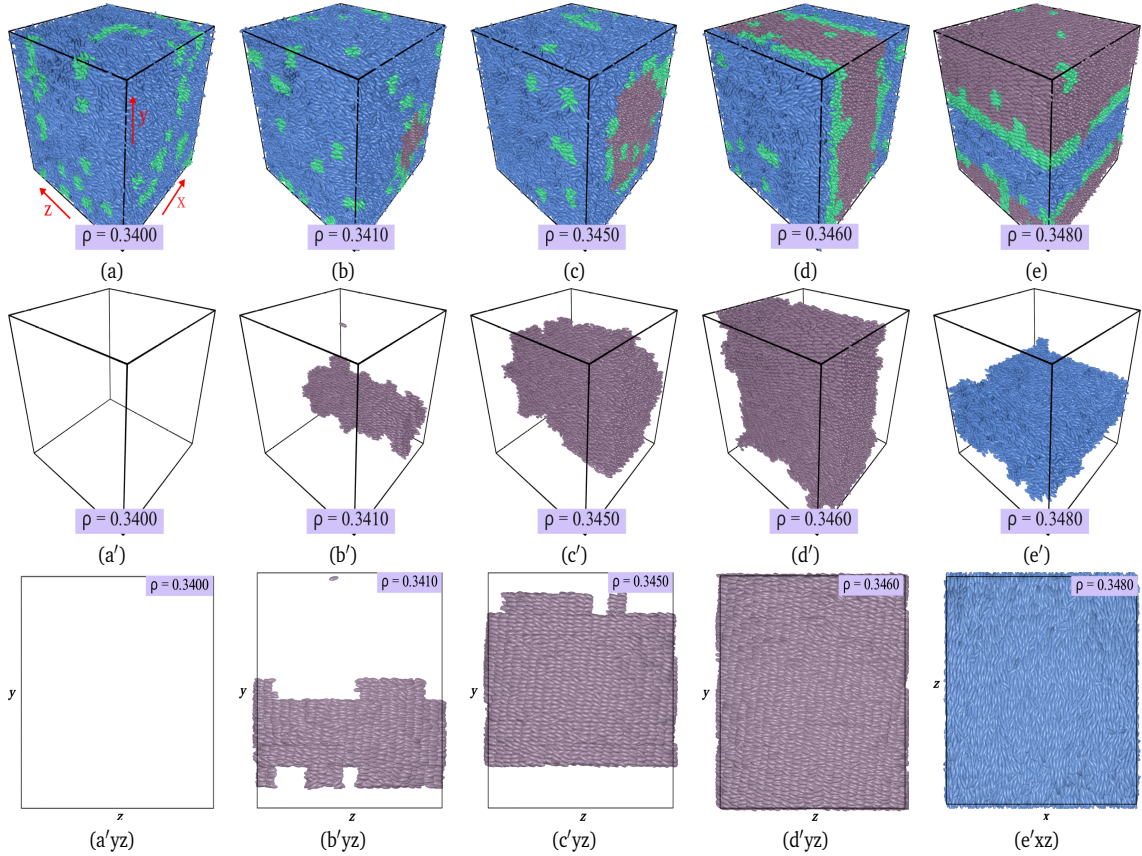


Figure 5.4: The snapshots exhibit the whole system and droplet with different viewing angles at lower nm-smB coexisting number densities for smaller system size, $L = 55.4921$. The nematic phase, smectic-B phase, and the nm-smB interface are represented in blue, pink, and green colors, respectively. Here, in a column, the images in the top row represent the whole system (i.e., the nm phase, smB phase, and nm-smB interface), and the second and third rows show only a single phase (nm or smB) at different viewing angles. The single-phase images are labeled by a prime symbol corresponding to the image shown in top row, such as (a'), which shows only the droplet formed in the system shown in (a). In the third row, the planar view of the droplet is shown for a better view of the droplet's phase, and the labeling of the third-row images includes the plane-of-view and the prime symbol. For instance, the image label (a'yz) indicates the droplet formed in the system shown in (a) viewing with the yz -plane-of-view

scenario (Fig. 5.5(b)), the method would identify the central sub-box as a droplet but may not recognize the nearby sub-boxes as a part of the droplet. Similarly, the droplet shown in Fig. 5.5(c) may also not be recognized as the sub-boxes only share a small portion of the droplet. Therefore, the droplets occupying a small portion of the sub-box may remain unidentified by our local-averaging identification technique.

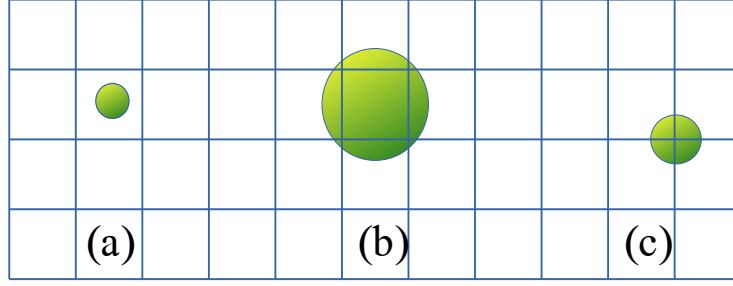


Figure 5.5: A cartoon picture shows different scenarios of a microscopic droplet formed in a simulation box divided into small sub-boxes

Further, at $\rho = 0.3410$ (Figs. 5.4(b), 5.4(b'), and 5.4(b'yz)), a cylindrical smB droplet emerges from the surrounding nm phase. However, in the solid-liquid coexistence for spherical particles, the spherical, cylindrical and planar (slab-like) droplets were found [14, 345]. Therefore, one would expect the sequence of the droplet's shapes in LCs upon increasing the number density to be aspherical, cylindrical, and planar. However, our simulation results indicate that a smectic aspherical cluster is not stable for the number density and the system we considered. It might be due to two reasons. One might be due to the similar direction of nm and smB directors. Experimental evidence shows that the orientational order dominates the phase separation more than the translational order [346]. However, in the case of nm-smB coexistence, there is no large difference in the orientational order between the two phases. Therefore, the smB aspherical droplet remains unstable in the system we considered, and the smectic phase grows along its director, resulting in a cylindrical droplet. Another reason might be the stronger effect of the highly ordered smB phase than that of the less ordered nm phase. As a result, less surrounding pressure due to nematic fluid does not hinder the smectic phase from expanding and forming a cylindrical droplet. To understand these results, a larger system size or higher aspect ratio could be helpful. These cylindrical smectic droplets are further observed for $0.3410 \leq \rho \leq 0.3450$ and the radius of curvature of these cylinders increases with ρ (as shown in Figs. 5.4(b') and 5.4(c')). However for $0.3460 \leq \rho \leq 0.3490$, the nm-smB interface is found to be planar where the width of the smB phase continuously

increases with ρ (see Figs. 5.4(d), 5.4(e), 5.4(d') and 5.4(e')).

With a further increase in ρ , the number of particles having both the positional and orientational order increases. As a result, the smB phase grows at the cost of the nm phase at higher densities. We expected the nm droplet to follow a similar but reverse trajectory upon increasing density as observed for the smB droplet at lower densities (i.e., from slab to cylindrical to no droplet). After the planar nm-smB interface, a cylindrical nm droplet is observed for $0.3500 \leq \rho \leq 0.3520$ (Figs. 5.6(a), 5.6(a') and 5.6(a'yz)). However, at $\rho = 0.3530$, an nm aspherical cluster surrounded by the smB phase is obtained (see Figs. 5.6(b), 5.6(b') and 5.6(b'yz)), which indicates that, unlike the smB droplet, an aspherical nm cluster can be stable in the smB phase. We believe that the stability of the aspherical nm droplet could be due to higher surrounding pressure by the highly ordered smB phase on the less ordered nm droplet such that the nm droplet could not expand to cylindrical at the given density. Upon further increase in the density, the nm cylindrical droplet is again observed at $\rho = 0.3540, 0.3560$ and 0.3570 (Figs. 5.6(d), 5.6(d') and 5.6(d'yz)) and no nm droplet is found at $\rho = 0.3550$ (Figs. 5.6(c), and 5.6(c')). For densities greater than the nm-smB coexisting density range (within the error bar), i.e. at $\rho = 0.3580$ and above, the smB phase occupies the whole system without any nm droplet (Figs. 5.6(e), and 5.6(e')). This is to emphasize that the elongation axis of the aspherical nm and smB droplets is along the nm and smB director, respectively (Fig. 5.4), which has been observed in various studies [55, 58, 338]. The cluster elongation along the preferred direction enhances their preferred interface surface area [24]. Also, as seen in the images (Fig. 5.4), the nm and smB directors are nearly parallel for all densities.

Several observations from simulations of the smaller system size indicate the relevance of incorporating the system-size effects in nucleation studies. First is the absence of smB aspherical droplet within the nm phase at lower densities. The second is the dissolution of nm droplet at higher densities. For instance, no nm

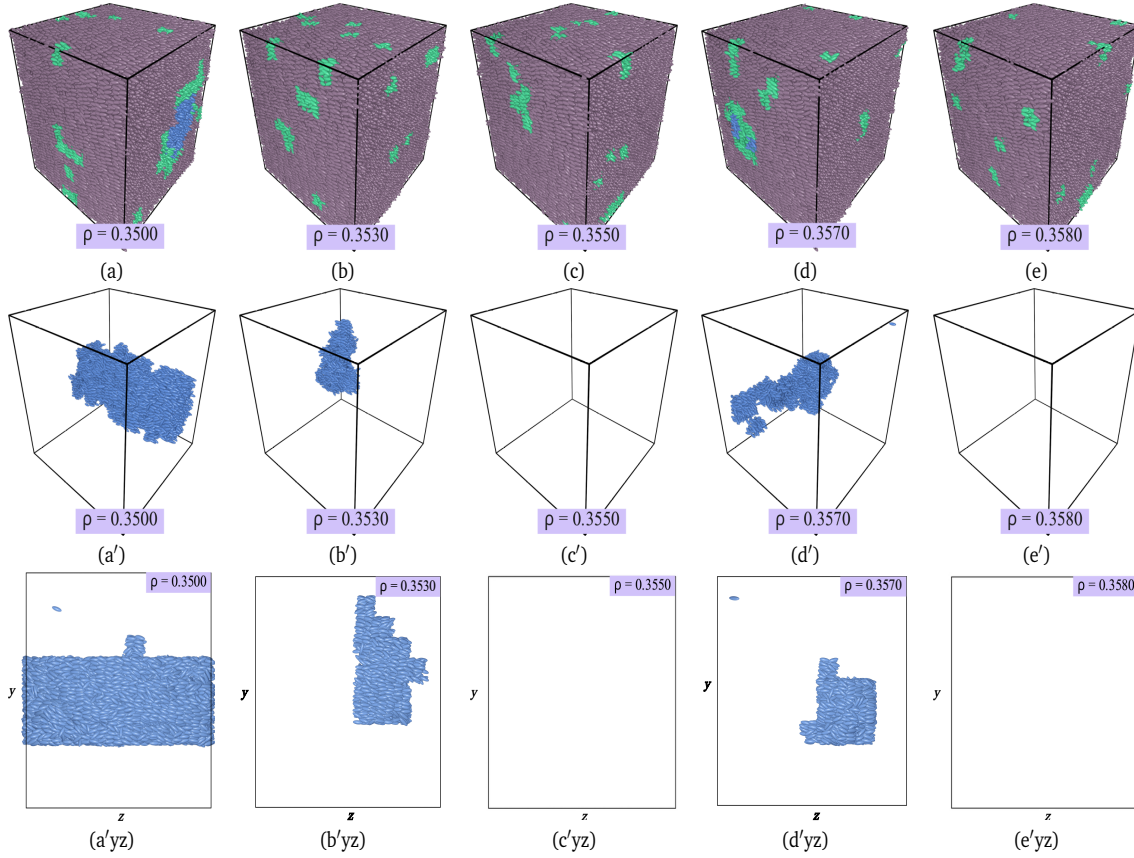


Figure 5.6: The snapshots exhibit the whole system and droplet with different viewing angles at higher nm-smB coexisting number densities for the smaller system size. Other descriptions of the images are the same as in Fig. 5.4

droplet is observed at $\rho = 0.3550$, possibly due to our local-averaging identification method (as discussed earlier). Further inspection of the system at $\rho = 0.3550$ reveals that the size of the central cuboid (nm in smB), taken in the second step of our recipe (see the sec. 5.2), may affect the results. When we ran the simulations with a smaller central cuboid, we observed the nm-smB coexistence with an nm cylindrical droplet (results are not shown here). But, the droplets' morphology is not influenced by the central cuboidal size, i.e., we will get the aspherical, cylindrical, and slab-like droplets. Therefore, depending upon the system size, the size of the central cuboid taken in our simulation recipe can influence the emergence or dissolution of the droplets. Such a non-stability of droplets due to finite-size effects indicates the importance of thermodynamic limit in nucleation studies. Hence, we have also

simulated a larger system size with $L = 97.1956$.

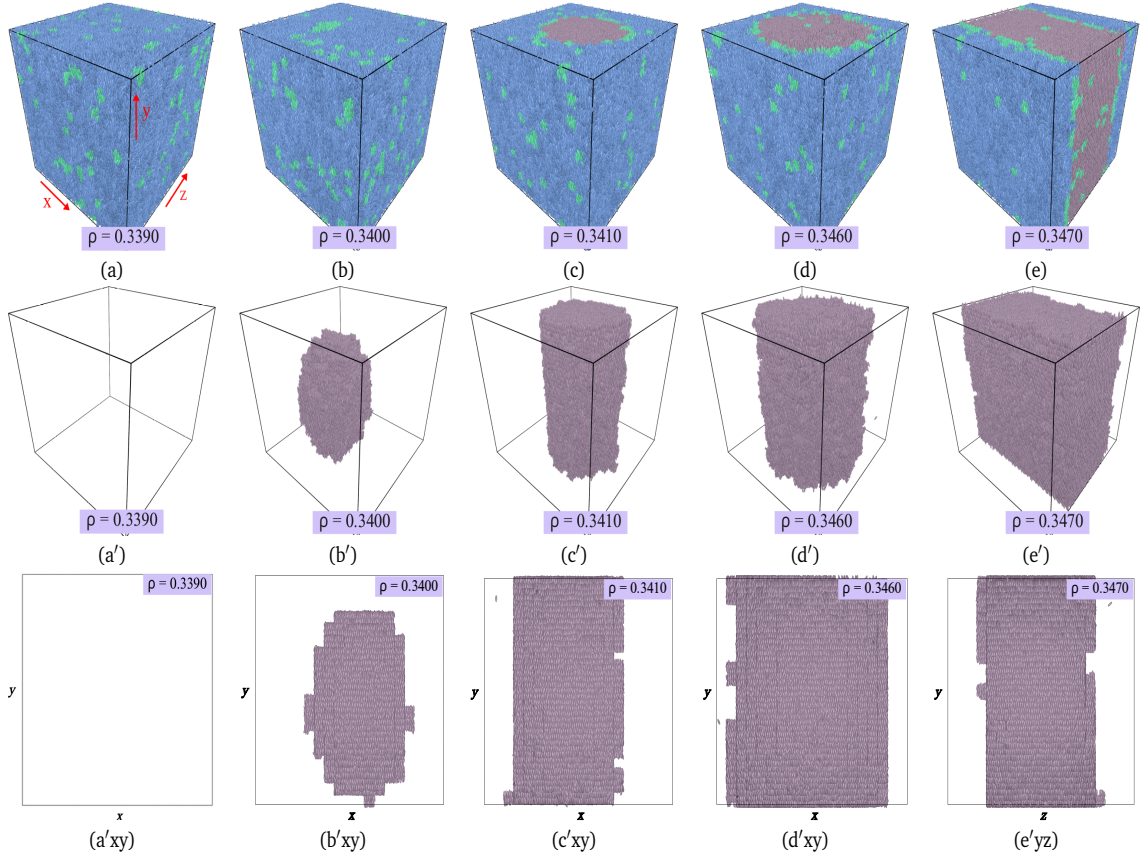


Figure 5.7: The snapshots exhibit the whole system and droplet with different viewing angles at lower nm-smB coexisting number densities for larger system size, $L = 97.1956$. Other descriptions of the images are the same as in Fig. 5.4

For larger system size, the simulations begin with $\rho_{nm}^f = 0.3340$ where the nm phase occupies the whole system without any smB droplet for $\rho \leq 0.3390$ (Figs. 5.7(a), and 5.7(a')). As discussed earlier, it could be due to finite system size or the local-averaging method used for the identification. Then, an aspherical smB cluster surrounded by the nm phase appears at $\rho = 0.3400$ (Figs. 5.7(b), 5.7(b') and 5.7(b'xy)). This result is in contrast to that of the smaller system size, reflecting the effect of system size on interfacial studies. Then, similar to the smaller system size, the cylindrical smB droplet is found at densities $0.3410 \leq \rho \leq 0.3460$ (Figs. 5.7(c) and 5.7(d)) and the radius of curvature of these smB cylinders increases with ρ (Figs. 5.7(c'), and 5.7(d')). Further, for $0.3470 \leq \rho \leq 0.3500$, the planar nm-smB

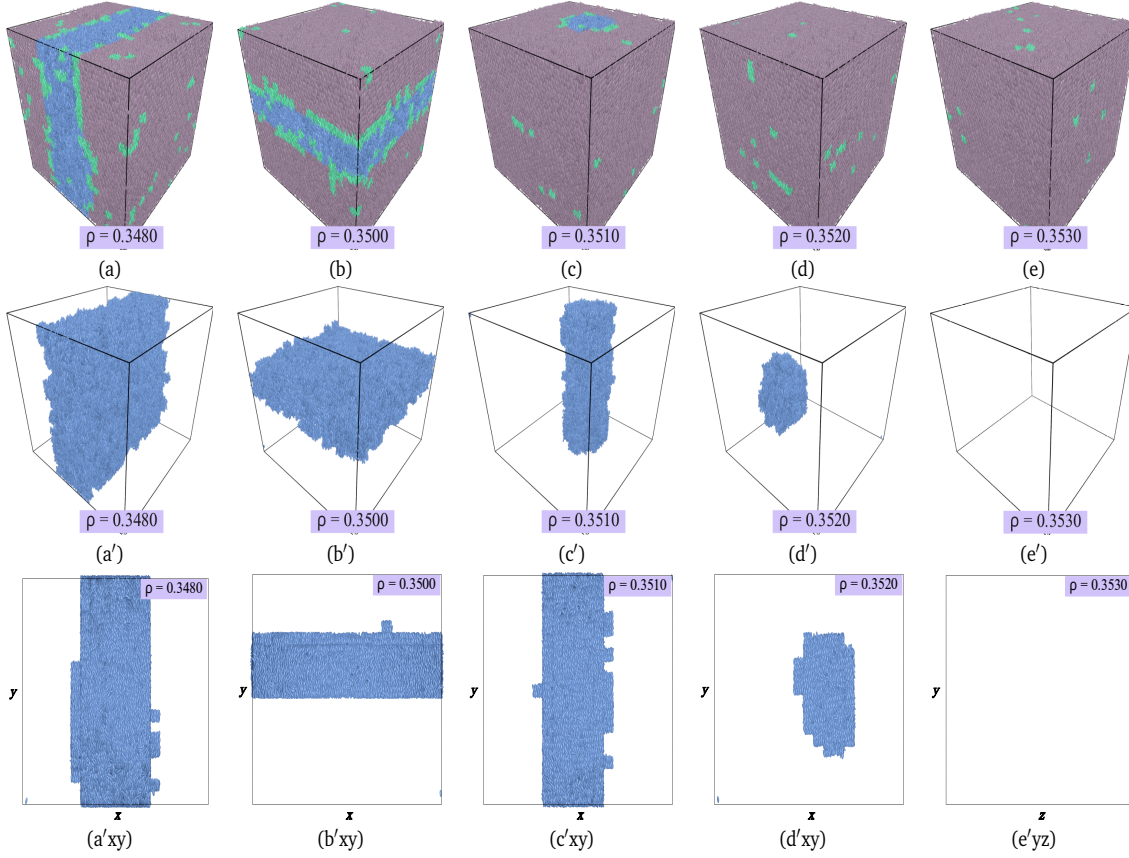


Figure 5.8: The snapshots exhibit the whole system and droplet with different viewing angles at higher nm-smB coexisting number densities for larger system size, $L = 97.1956$. Other descriptions of the images are the same as in Fig. 5.4

interface is observed with the growing smB and depleting nm phase widths upon increasing ρ (Figs. 5.7(e), 5.8(a)) and 5.8(b)). Then, the cylindrical nm droplet and an aspherical nm cluster appear at $\rho = 0.3510$ and $\rho = 0.3520$, respectively (Fig. 5.8(c), and 5.8(d)). For larger system size, the nm-smB coexistence vanishes at $\rho \geq 0.3530$, and the smB phase appears in the whole system without the formation of any nm droplet (Fig. 5.8(e), and 5.8(e')). During the coexistence, the elongation of droplets is found to be along the nm or smB director, as is observed for the smaller system size. Also, the nm and smB directors are nearly parallel for all densities. To sum up, the nm and smB phases formed in the GB system can coexist with each other, separated by aspherical, cylindrical, and planar interfaces within the nm-smB coexistence region.

5.4 Summary and conclusion

This chapter presents the morphology of nm and smB droplets formed within the nematic-smectic B coexistence region for the GB (3, 5, 2, 1) system. The nm-smB phase coexistence is obtained by using our *three-step recipe* (sec. 5.2). We found that identifying the nm or smB droplets formed in the nm-smB phase coexistence is not straightforward. First, we used a particle-based identification strategy (q_6q_6) to distinguish between nm and smB phases. However, this technique could not locate the non-planar nm-smB interfaces formed in our present work (though we have used the same in our previous work [341] where the nm and smB phases were separated by a planar interface). Therefore, due to the inadequacy of such a particle-based strategy, we have developed a local-averaging technique to identify the nm and smB phases. In this technique, we have calculated the sub-box orientational order parameter (S_{sb}) in small sub-boxes of the simulation box. Then, the sub-box orientational order distributions are plotted, which confirm the coexistence of two phases (Figs. 5.1, and 5.2). Using these distributions, we have got an identification criterion that the sub-boxes having $S_{sb} < 0.8$ contain the nm phase, and $S_{sb} \geq 0.9$ have the smB phase. The sub-boxes with the intermediate values in the range of $0.8 \leq S_{sb} < 0.9$ can have either the nm-like or smB-like phase and, thus, form the nm-smB interface. This identification criterion has successfully identified the nm and smB phases in the present study and provided a rough view of the droplets' morphology within the nm-smB phase coexistence. The simulation results with two different system sizes have given us an insight into the finite system size effects on the nm-smB phase coexistence. In both the systems, the nm and smB phases coexist with each other, separated by aspherical, cylindrical, and planar interfaces (shown in Figs. 5.4, 5.6, 5.7, and 5.8). With the smaller system size, though, the aspherical nm-smB interface is found only with an nm droplet inside the smB phase; the reverse, i.e., an aspherical smB droplet inside an nm phase, is not observed. For the latter case, the system size could be the reason for not getting an aspherical smB droplet

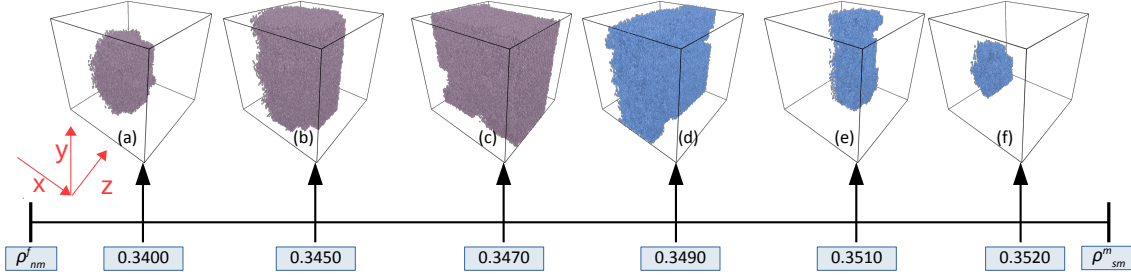


Figure 5.9: One-dimensional morphology diagram along the nm-smB phase coexistence line for GB LC material. As the overall density (ρ) of the system increases from $\rho_{nm}^f = 0.3340$ to halfway within the nm-smB coexistence region, the smB droplet surrounded by the nm phase changes its shape as (a) aspherical $\rightarrow$ (b) cylindrical $\rightarrow$ (c) slab. Upon further increase in ρ up to $\rho_{sm}^m = 0.360$, the nm droplet surrounded by the smB phase changes its shape as (d) slab $\rightarrow$ (e) cylindrical $\rightarrow$ (f) aspherical

such that the more ordered smB phase grows and results in a cylindrical droplet surrounded by the less ordered nm phase. However, the stability of an aspherical nm droplet within the smB phase at higher densities might be due to the difficulty for the less ordered nm phase growing through the more ordered smB phase. In contrast, the aspherical nm droplet inside the smB phase and the aspherical smB droplet within the nm phase are observed for the larger system size. These results indicate the significance of including the finite-size effects for efficiently understanding the nucleation phenomenon. For both the system sizes, the elongation of droplets is nearly parallel to the nm and smB directors, which has been observed in various studies for the isotropic-nematic phase transition [67, 68, 337]. Finally, Fig. 5.9 summarizes our findings as a one-dimensional morphology diagram along the nm-smB phase coexistence line for GB LC material. In conclusion, the present study has given us an overview of the possible shapes of GB nm and smB droplets formed within the nm-smB phase coexistence.

Chapter 6

Summary and concluding remarks

This thesis presents the study of the interfacial phenomenon in liquid crystalline material using the molecular dynamics simulation technique. The MD simulations are performed using the LAMMPS package by considering the Gay-Berne interaction potential between LC ellipsoids with $(3, 5, 2, 1)$ GB parameters. The GB system is studied with and without confinement. In the case of an unconfined GB system, the stiffness of an interface formed between nematic (nm) and smectic-B (smB) phases is computed using capillary wave theory (as reported in Chapter 3). Using density profiles across the interface, the range of nm-smB coexisting densities is calculated, which comes out to be $\rho_{nm}^f = 0.334 \pm 0.002 < \rho_{co} < \rho_{sm}^m = 0.360 \pm 0.002$. This finding fulfills the first objective of this thesis. The coexisting nm and smB phases separated by a planar interface are identified using a particle-based (microscopic) local bond order parameter, i.e., $q_6 q_6$. The directors of the nm and smB phases are nearly parallel to each other and perpendicular to the interface normal. The nm-smB planar interface is found to be rough, which is anticipated due to the small aspect ratio (i.e., $\kappa = 3$) of the GB ellipsoids. Using CWT analysis, the stiffness of the nm-smB interface is found to be $\tilde{\gamma}_{nm-smB} = 0.399 k_B T / \sigma_{ee}^2 = 0.044 / \sigma_{ss}^2$ for the planar anchoring of nm and smB directors at the interface. This study can be further extended by simulating the GB LCs of aspect ratio higher than 3. Hence, the

effect of particle elongation on the nm-smB interfacial roughness can be explored, and the applicability of CWT for longer GB ellipsoids can be tested. However, to that end, efficient computational methods need to be developed to obtain the nm-smB coexistence for longer GB ellipsoids, as the equilibration of such a system (with longer GB ellipsoids) would be challenging to achieve. Furthermore, the nm-smB interfacial properties with non-planar anchoring also need to be explored.

In addition to the unconfined GB system, the interfacial tension of the interfaces formed in a GB LC system confined by two soft-smooth-repulsive WCA walls is also determined, as reported in Chapter 4. By observing the simulation snapshots, pressure tensor profiles, and the orientational order parameter near the walls, we found that the mechanical anisotropy introduced by WCA walls to the system is very small at lower densities. Hence, the interfacial tension for the wall-isotropic fluid interface is less at low densities. However, with an increase in density, the walls influence the particles to arrange themselves in the smectic layers near the walls with the homeotropic anchoring (Figs. 4.1, 4.4, and 4.6). The homeotropic alignment gets stronger near the wall with density, as observed from the stronger oscillations in the transverse component of pressure (Figs. 4.2 and 4.5) and the orientational order parameter calculated near the wall (Fig. 4.3). The interfacial tension (γ_{WI}^*) of an interface formed between GB isotropic fluid and WCA wall is determined using the pressure tensor method. γ_{WI}^* is found to increase with ρ until strong smectic layers are formed next to the wall (Fig. 4.8). Afterward, γ_{WI}^* starts decreasing because the smectic layers formed near the wall induce further wetting, thus reducing the energy required to form an interface. Here, the finite-size effects are also analyzed, but we observed no significant dependence of γ_{WI}^* on the system sizes we considered. However, γ_{WI}^* is found to be dependent on the wall-particle interaction strength ϵ_W (Fig. 4.9), such that the higher the ϵ_W , the higher the γ_{WI}^* . Upon increasing ϵ_W , γ_{WI}^* increases to a density close to the isotropic-nematic phase transition density. Afterward, γ_{WI}^* starts reducing, possibly due to increased agita-

tion among the particles. A thorough analysis of bulk behavior at higher densities, including the isotropic-nematic phase transition density, is still required. Moreover, the interfacial properties in the confined GB system with higher aspect ratios of ellipsoids and different wall properties, such as different wall-particle interaction potential and microscopic structures, can also be investigated. The findings described above, regarding the properties of the nm-smB and wall-isotropic fluid interfaces in the GB LC material, address the second objective of this thesis.

We have also studied the morphology of GB nematic and smectic-B droplets formed within the nm-smB phase coexistence (as discussed in Chapter 5). The nm-smB phase coexistence is achieved using a *three-step recipe* (refer to sec. 5.2). The identification of coexisting nm and smB phases is done by developing a local-averaging method based on the orientational order parameter. This method calculates the orientational order parameter in small sub-boxes of the simulation box (S_{sb}). Then, the S_{sb} distributions are plotted, which confirm the nm-smB phase coexistence (Figs. 5.1 and 5.2). An identification criterion is developed using these distributions, such that the sub-boxes with $S_{sb} < 0.8$ have the nm phase, and the sub-boxes with $S_{sb} \geq 0.9$ contain the smB phase. The sub-boxes with intermediate values, such as $0.8 \geq S_{sb} > 0.9$, represent the nm-smB interface. Using the sub-box orientational order criterion, we have found the aspherical, cylindrical, and planar shapes of nm and smB droplets formed within the nm-smB coexistence (shown in Figs. 5.4, 5.6, 5.7, and 5.8). Thus, the local-averaging identification technique has helped us to distinguish between nm and smB phases and provided a rough view of the droplets formed within the nm-smB phase coexistence. However, the actual behavior of coexistence can only be captured in the thermodynamic limit, so to address this, we have analyzed our simulation data for two different system sizes. Several observations with the smaller system size differ from those with the larger one. These results indicate the relevance of including the finite-size effects to understand the interfacial phenomenon better. For both the system sizes, the

elongation of aspherical droplets is nearly parallel to the nm and smB directors. These results, showing the morphology of homogeneous nm and smB droplets, fulfill the third objective of this thesis. This work can be further extended by calculating the chemical potential and the free energy difference required for stabilizing the nm and smB droplets. Moreover, the effect of the aspect ratio on the droplet's morphology would also be interesting to check. Apart from the purely academic interest regarding the nucleation phenomenon in LC materials, understanding such interfacial phenomenon is crucial for better processing of LC materials due to their vast industrial applications, such as biosensors, functional materials, etc.

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