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Abstract

In this thesis, the nucleation phenomenon in ⁴thermotropic liquid crystalline material is investigated using the Molecular Dynamics (MD) simulations technique. The interaction between the liquid crystalline (LC) particles is modeled by using the Gay-Berne (GB) potential model. To understand the interfacial phenomenon in GB LCs, the properties of the interfaces formed in unconfined and confined GB LC system are calculated. Due to the inadequate studies on the nematic-smectic B (nm-smB) interface in the literature, we have mainly focused on analyzing the interfacial phenomenon with nematic (nm) and smectic-B (smB) phases.

For the unconfined GB system, the interfacial stiffness of the nm-smB interface has been 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 or smB droplets formed within the nm-smB coexistence is also analyzed. For the identification of co-existing nm and smB phases separated by planar and non-planar interfaces, we have developed a coarse-grained technique based on the orientational order parameter. This identification criterion has helped us to determine the aspherical, cylindrical, and planar shapes of nm and smB droplets formed.

The confinement of isotropic GB fluid by the soft, smooth, and repulsive walls is also studied. The interaction between GB particles and walls is defined by the Weeks-Chandler-Anderson potential (WCA) potential model. ⁴Using the pressure-tensor method, the interfacial tension between GB isotropic fluid and WCA walls is determined. ⁴The effect of the wall-particle interaction strength on the interfacial tension between WCA wall-GB isotropic fluid is also analyzed. The finite-size effects on the interfacial properties and the droplet morphology are also studied.

Thesis layout

This thesis consists of six chapters which are arranged ³² 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 or wetting phenomenon in materials containing spherical particles. The interfacial studies in liquid crystalline materials for different interfaces, such as isotropic-nematic, isotropic-smectic, and nematic-smectic interfaces, are reviewed. ⁹ 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 with the free energy expression 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 detailed expressions used for the potentials to model the LC particle-particle interaction (Gay-Berne potential) and the LC particle-wall interaction (Weeks-Chandler-Anderson potential) are given. Our main focus ⁹⁸ in this work is to determine the interfacial properties in GB LCs, such as interfacial stiffness or tension. The theoretical methods used to compute the interfacial properties, such as CWT and PT method, are briefly described in this chapter.
- In **Chapter 3**, the MD simulation results of the GB ellipsoidal particles in a cuboidal box are presented. Using GB (3, 5, 2, 1) model parameters, we have been able to observe the nematic-smectic B (nm-smB) phase coexistence. By analyzing the coexisting phases' density profiles along a direction transverse to the interface, the nm-smB phase coexistence range is calculated. Using the

local bond order parameter q_6q_6 , the particles belonging to the nematic and smectic-B phases are distinguished. As a result, 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 ¹⁰walls for a wide range of number ⁴densities 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 bulk isotropic (I) phase and WCA wall at various number densities (ρ) is calculated. In addition, ⁴the effect of the system-size and the wall-GB interaction strength on the wall-GB interfacial tension is also presented.
- In **Chapter 5**, the possible droplet shapes formed within the nm-smB phase coexistence region are analyzed by taking the GB liquid crystalline molecules in a finite cuboidal box. Different morphologies of the homogeneous nematic (nm) or smectic-B (smB) droplet formed in the smB or nm phase, respectively, are observed at different number densities (ρ). To identify the nm and smB phases, we have developed a novel coarse-grained 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 got an identification criterion to identify the nm or smB phase. Using such a coarse-grained method, the aspherical, cylindrical, and planar shapes of nm and smB droplets are observed within the nm-smB coexistence. ⁴⁶The effect of finite-system size on the morphology of these droplets is also shown.
- At the end, in **Summary** chapter, the results drawn from our study, as discussed in the above chapters, are summarised. Additionally, the future scope that comes out 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] phenomenon. The nucleation phenomenon is defined as generating a new thermodynamically stable phase from a metastable mother phase through self-assembly or self-organization. It can be observed in various industrial, technological, biological, natural, and household activities [4,5]. 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. The nucleation phenomenon is broadly categorized into two types, namely homogeneous and heterogeneous nucleation. The emergence of a droplet of a new phase spontaneously from a moderately supersaturated mother phase via statistical fluctuations is known as homogeneous nucleation. 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. The origi-

nal theory to understand homogeneous nucleation ⁵¹ is the classical nucleation theory (CNT) [6]. According to CNT, the small nuclei of the new phase formed, due to the thermal fluctuations, disappear or grow if the fluctuations are small or large, respectively. As these nucleating nuclei grow, they become stable if they achieve a critical size; otherwise, they might shrink and dissolve in the mother phase. Beyond the critical size, the nucleus of the new phase generally grows faster than the rate at which it forms. The emergence rate of these critical nuclei is known as the nucleation rate, which determines the time required for a phase transition to occur. The basic assumptions taken in CNT are very simple, but they are not valid under many circumstances (discussed briefly in chapter 2). Therefore, CNT has several limitations [2,3,7] and many new approaches have been developed for the critical understanding of the nucleation phenomenon [8]. Some examples of such non-CNT approaches are the density-functional approach [9], semiphenomenological model, and Fisher's model [6]. The phase transitions occurring via the nucleation phenomenon are of the first-order type and thus have to cross a kinetic barrier. Various observations indicate the presence of kinetic barrier such as the cooling of highly purified tiny water droplets in capillary tubes below -30°C without freezing, the undercooling of emulsified gallium droplets for 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 [8], and thus, an observer has to wait for eventuality to observe a nucleation event. Therefore, such rare events are tedious to study using conventional simulation techniques because it involves a lot of CPU time. Consequently, elementary models such as the Ising model, and a very large supersaturation having a few $k_B T$ of nucleation barrier [10,11,12,13] have been used to study the nucleation kinetics using simulations. Various ⁸simulation techniques have been used to investigate the nucleation phenomenon such as transition-path-sampling, umbrella-sampling, or forward-flux-sampling methods [14], Monte Carlo (MC) [15,16] and Molecular Dynamics (MD) [6,17,18,19] simulations. Among various techniques, Molecular Dynamics (MD) technique provides a valuable alternative to observe the

SECTION 1.1: NUCLEATION OR SPINODAL DECOMPOSITION

nucleation event directly. Hence, MD has been widely used to investigate the nucleation phenomenon in different model systems [20]. 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 or spinodal decomposition

Before applying the nucleation theory, it is important to know whether the phase separation occurs via nucleation-and-growth or spinodal decomposition. When a system is ¹⁵ quenched into a state with at least one unstable order parameter, the phase separation occurs through spinodal decomposition [21]. In this case, the small amplitude fluctuations make the initial homogeneous system unstable, due to which phase separation occurs ¹⁵ immediately after a quench. During the spinodal phase separation, an interconnected labyrinth structure of regions, with lower and higher order, is initially formed. However, if a system reaches a metastable state after a quench, then phase separation occurs due to sufficiently large amplitude fluctuations. These fluctuations have less probability of occurrence because the phase separation starts ¹⁵ after a certain delay time, known as the induction or latency time. This is the nucleation and growth phenomenon in which the nuclei are initially generated throughout the volume and grow only if they achieve a sufficiently large size. In high-temperature solids, the spinodal appeared unexpectedly near the equilibrium melting point (tens of degrees above), which largely affected the nucleation rates and considerably hampered the superheating of crystals [8]. Onsager [22] showed that the situation for spinodal and nucleation is different for the aspherical particles, i.e., disc-shaped or elongated particles, in a liquid crystalline system. Here, the orientational fluctuations determine the unstable or metastable state of the system and result in phase separation due to the concentration differences. The liquid crystalline isotropic-nematic spinodal or binodal decomposition has been well studied ([21,23,24] and refs. therein). Depending upon the preparation of the initial state (i.e., isotropic or nematic), quenching can lead to different phase separation kinetics. For

instance, with an initial isotropic state, the ⁶spinodal decomposition occurred at high concentrations, and nucleation-and-growth was observed at lower concentrations ²¹. However, this was reversed with an initial nematic state ²¹. Moreover, the cessation of the ¹⁵external fields such as shear flow, magnetic field, etc. can also lead to phase separation ²¹.

1.2 Nucleation in materials composed of isotropic particles

There are various theoretical, experimental and simulation studies which have investigated the mechanism of homogeneous nucleation ^{17,9,10,25,26}. 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 upon the degree of undercooling or the ⁶¹free energy difference between the two phases. The third stage involves the coalescence of larger droplets. The nucleation phenomenon in the case of spherical particles is widely studied using computer simulations ²⁷ and theoretical means ^{8,28,14}. These studies found that the structure at the core of the central nucleus might vary completely from the new bulk phase formed. Also, the interface between the critical nucleus and the metastable state may be represented by a ⁸density and structural profile which is not sharp, and step-like ^{14,27,8,28}. The condensation process (i.e., gas-to-liquid transition) occurs with the formation and expansion of molecular clusters and has been well studied using Volmer's classical theory, Mayer's theory of condensation, etc. ²⁹. During the vapor-liquid coexistence in LJ fluid, different shapes of homogeneous vapor or liquid droplets have been observed ^{10,30}. To understand the morphology of droplets formed, Schrader *et al.* ¹⁰ plotted the chemical potential (μ) versus density (ρ) as shown in Fig. ^{1.1}. In a finite cubical box, $\mu = 0$ at $\rho = \rho_l$ or $\rho = \rho_v$ correspond to the homogeneous liquid or vapor phases, respectively, which can coexist with each other in the thermodynamic limit. The vapor or liquid phases can be found at $\rho > \rho_v$ or

SECTION 1.2: NUCLEATION IN MATERIALS COMPOSED OF ISOTROPIC PARTICLES

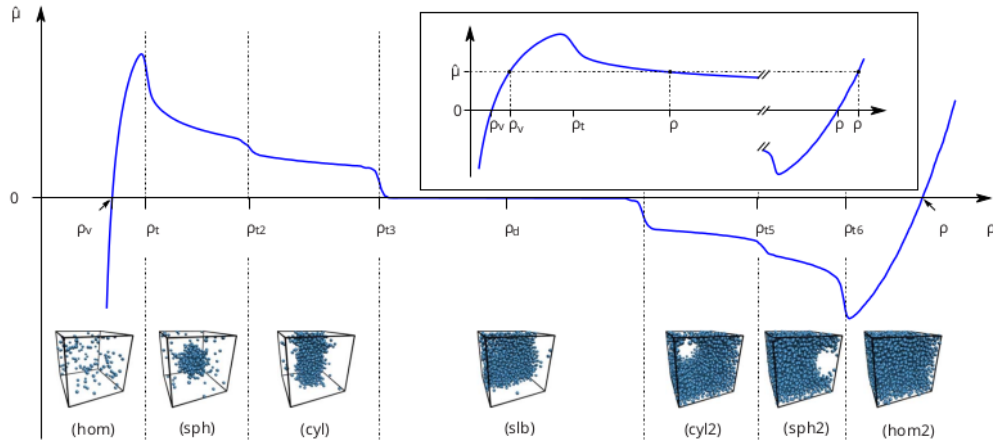


Figure 1.1: The plot of chemical potential versus density describes the morphology of droplets formed in the case of Lennard-Jones fluid as reported by Schrader *et al.*, *Phys. Rev. E* **79**, p. 061104 (2009) [10]

$\rho < \rho_t$, with $\mu \neq 0$, till the state of condensation or evaporation. A spherical liquid droplet coexisted with the supersaturated vapor when the system density exceeded the condensation density. Further increase in density converted the spherical droplet into a cylindrical droplet which sustained within the vapor. In the central region with $\rho = (\rho_l + \rho_v)/2$, the coexistence was found with a slab configuration. After the slab configuration, the droplet character was reversed. Therefore, upon a further increase in density, first, a cylindrical and then spherical-shaped bubble coexisted with liquid. At further higher densities, the stable homogeneous liquid phase was formed. In addition to this simple two-phase coexistence, it was also shown (in [10]) that for $\mu > 0$, three states having the same value of μ , such as a homogeneous vapor, coexisting homogeneous liquid droplet with the vapor, and a homogeneous liquid, can coexist with each other [10].

The solid-liquid nucleation has also been well investigated in various studies [31]. The crystallization process occurs via two steps: firstly, a critical-sized crystallite nucleates from the liquid, and further grows to macroscopic dimensions. As the crystal grows rapidly, only the nucleation rate, in the first step, controls the freezing rate of an undercooled liquid. Due to such a rapid crystal growth, the critical nucleus can not be directly studied. Therefore, it gets difficult to experimentally measure

the minimum temperature required to supercool the small liquid droplets before crystallizing. In consequence, significant corrections were found by conducting more experiments [31] in the original extensive temperature measurements by Turnbull [26] for various liquid metals. During the isotropic-crystal coexistence, 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. As the thermal energy of the isotropic liquid is higher than that of a crystalline solid, a crystal would have to gain some energy to convert it into a liquid. On the other hand, a liquid would have to lose some energy to become a crystal. This results in a nucleation ²²barrier that needs to be overcome for the nucleating crystals to grow. Because of this competition among particles, the interface appears like a capillary wave, and the corresponding theoretical framework is called the capillary wave theory (CWT). At the coexistence pressure, P_{co} , solid and fluid coexist in equilibrium, and there is no thermodynamic force to drive the system away from coexistence. As a result, the system 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 [32,33] in the case of spherical colloidal particles.

Apart from homogeneous nucleation, the presence of a nucleation site, such as an impurity or surface, leads to fascinating surface phenomena such as adsorption, wetting (nucleation), etc. The heterogeneous nucleation or wetting occurs much more often and thus is easily observed. Several technologies, namely gluing, coating, dyeing, etc., are based ²²on 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 studied in various model systems [3] resulting in spherical cap-shaped droplets [34]. Therefore, a considerable amount of empirical knowledge of the nucleation phenomenon has been gained in a system of isotropic particles. However, in nature, there are also molecular materials made up of aspherical particles, such as liquid crystalline material. The shape

SECTION 1.3: LIQUID CRYSTALLINE DROPLETS

anisotropy of particles in liquid crystalline material makes the phase diagram rich and interesting [35,36,37,38,39,40]. Therefore, the study of interfacial phenomenon in liquid crystals leads to interesting interfacial properties. In this thesis, we have presented the study of the nucleation or interfacial phenomenon in thermotropic calamitic (elongated) liquid crystals (LCs). The thermotropic LCs exhibit several phases upon changing the temperature, such as isotropic, nematic, smectics, crystalline etc. (Fig. 1.2) [41]. 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 orientations of molecules (Fig. 1.2). In the smectic phase, the molecules orienting in a similar direction are arranged in layers. 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 is like the smA phase, but it has a hexagonal crystalline order in each layers which are not correlated. However, if these layers are locked like a (1, 1, 1) plane in fcc or hcp lattice, then a crystalline phase is formed. Such a rich phase behavior of LCs has helped them to find their use in technologically diverse applications [42,43,44,45,46,47,48] like LC displays, electrically controlled phase shifters, polarization rotators, optical switches, etc. Therefore to prepare suitable LC materials for their diverse applications, the precise material processing methodologies are required which would be developed with a better understanding of the nucleation and growth phenomena.

1.3 Liquid crystalline droplets

Majority of studies on anisotropic particles examined the nematic droplets as micro-domains in isotropic fluid [50] because they exhibit an interesting interfacial phenomenon. In contrast to nucleation in materials with isotropic particles, the nucle-

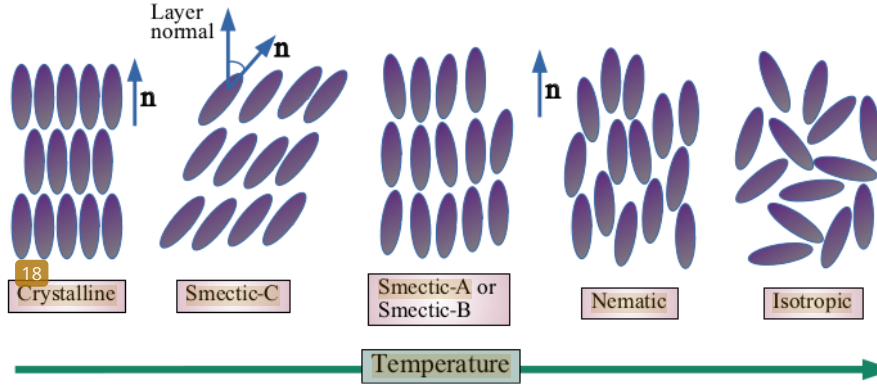


Figure 1.2: Different phases of thermotropic liquid crystals are shown, with the isotropic phase having no order and the nematic phase having only the orientational order. The smectic-A (smA) and smectic-C (smC) phases have particles arranged in layers with no positional order within the layers. However 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 it 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 fcc or hcp lattice, then a crystalline phase is formed (adapted from [49])

ation 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 nucleation of the nematic phase occurs via a phase ordering kinetic process [51] 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, eventually with time, the surface energy cost of the droplet decreases, which thermodynamically favors the nucleation of a sufficiently large droplet. 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 [52]. The isotropic or nematic droplets have also been observed during the melting of free-standing smectic films [53, 54]. These 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, which arose due to the surface energy gradients between the droplets [53].

SECTION 1.3: LIQUID CRYSTALLINE DROPLETS

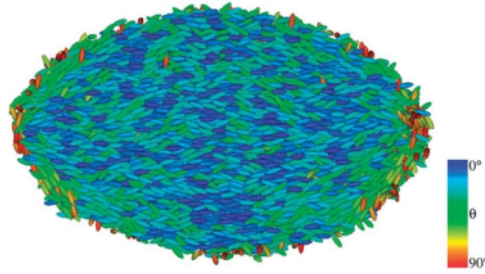


Figure 1.3: A nematic GB droplet in coexistence with its vapor phase. The color coding indicates the orientation (θ) of GB particles with respect to the droplet's principal inertia axis. The image is taken from the work done by Vanzo *et al.*, *Soft Matter* **8**, p. 11790-11800 (2012) [55]

In LC materials, their constituent aspherical particles having positional and orientational order may develop anisotropic clusters during the nucleation. 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 is often observed in the case of small-sized droplets [20]. Therefore, in contrast to other fluid systems, bulk properties overpower the interfacial effects in the case of smaller liquid crystalline droplets [20]. In other words, the distortion in the droplet shape can be due to the elastic deformation of the director field [56]. There are various studies which showed that the shape of LC droplets can deviate from circular or spherical [56] (Fig. 1.3). For instance, the study of nematic droplets in smectic membranes found large circular nematic droplets and small elongated droplets at low temperatures [56]. In contrast, 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 [57, 21, 23, 58] and simulation [59, 14] studies on the assembly of the nematic phase have resulted into the elongated spindle-shaped nematic droplets known as tactoids [23]. These tactoids can grow via Ostwald ripening [60] or coalescence [21, 61] to form Schlieren patterns [62]. The tactoid shape of droplets is due to free energy minimization. The tactoids exhibit different sizes and aspect ratios in the perturbed system [24].

However, the extremely elongated tactoids fill out during their growth to maintain a constant aspect ratio [24]. Regarding the droplet growth, some studies observed the droplet elongation along the particles' director [63,55,52,24,62] whereas others found the elongation direction different than of the director [64]. Furthermore, apart from using the simple fluid, the nucleation in the mixture of rods with the non-adsorbing polymer has also been well-studied [59,65] because the polymer addition instigates an effective attraction between the rods via the depletion attraction [59] and broadens the coexistence region. The smectic or crystalline droplets in LCs have also been investigated using experiments [65,66] and simulations [67,68], but simple transient droplets were not observed.

1.4 Crystallization in LCs

In contrast to spherical systems, the crystal nucleation pathways are more complicated in systems containing anisotropic particles [69]. The crystallization in the case of spherical particles results in roughly spherical crystal nuclei [67]. 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., ¹²parallel and perpendicular to the molecular axes, which leads to the aspherical ¹³²equilibrium shape of small crystal nuclei. Beyond the critical size of the crystals ¹²nuclei, 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 [67]. 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 [67]. 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 [68]. In an isotropic-to-crystal nucleation study of a

SECTION 1.4: CRYSTALLIZATION IN LCS

colloidal suspension of short hard spherocylinders (Fig. 1.4), self-poisoning occurred because the crystal nucleus, despite free of defects, was surrounded by a liquid layer of molecules aligned differently than the crystallite director [67]. Hence, the second-

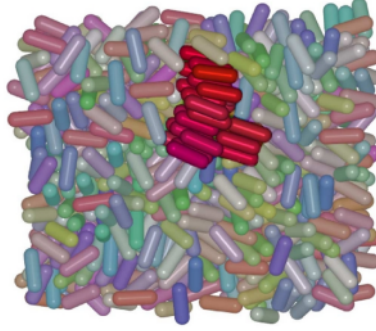


Figure 1.4: A crystalline cluster (red colored) in a metastable isotropic liquid was obtained in a fluid of hard spherocylinders by Schilling *et al.*, *Phys. Rev. Lett.* **92**, p. 085505 (2004) [67]. Schilling *et al.* [67] colored the particles differently according to their orientations

layer crystal growth was difficult because the particles needed to be prealigned to be added into the crystals, which cost free energy. Then a nucleation event was required to form a compact cluster to 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 [67][69]. 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 [66] or raft-like [70] crystallites [67]. The multilayer growth of the crystals can be facilitated by using an orientationally biased field, such as a strong and static magnetic field [67].
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 [69]. In LCs, particle anisotropy results in unique and complex interfacial properties. Therefore, the surfaces and interfaces in the liquid crystalline system have been well studied due to their practical applications in

liquid-crystal `display` devices [71,72]. Now, 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-nem interface, pressure is not considered an important parameter because both phases are incompressible. Moreover, the isotropic and nematic phases have small density differences, so it is believed that density does not influence the interfacial properties [73].

1.5 Isotropic-Nematic interface

During the iso-nm coexistence, the translational and the orientational symmetry are broken at the interface. The interfacial profiles can be analyzed by using the density and orientational order profiles [74,75,73,76]. The measurement of the interfacial width by fitting the hyperbolic tangent function to the simulated density profile have led to a good description of iso-nm [74] and nematic-vapor (nm-vap) interfaces [77,78]. The iso-nm interface has been widely studied using theoretical [51,73,79,75,80,79,81,82,83], experimental [84,85], and simulation methods [86,87,88,76,89,90,91]. The Onsager model [22] was considered an appropriate model for understanding the nematic ordering in liquid crystals [75]. For thermotropic LCs, the anisotropic Gay-Berne (GB) potential model [92] has been widely used to investigate the iso-nem interfacial properties [90,73,74], and liquid-vapor (isotropic-vapor or nematic-vapor) interface [55,77,78]. The iso-nem interfacial properties such as the interfacial width, tension etc. has been computed by various techniques in different systems such as by using spherical harmonic expansion for rod-like system [75,81], pendant drop technique for semiflexible polymer [93], scaling relation for phase-separated colloidal dispersions [80], free energy differences [94], pressure tensor method for repulsive ellipsoids [89], hard spherocylinders [82], hard and soft ellipsoids [95], finite-size analysis for soft repulsive spherocylinders [86], capillary wave spectrum for repulsive ellipsoids [89], variational method [96], and step-function density profile [97], etc. The interfacial properties might be influenced by the molecular interactions, capillary-wave undulations, and the coupled transla-

SECTION 1.5: ISOTROPIC-NEMATIC INTERFACE

tional and rotational degrees of freedom [95]. For instance, the iso-nm interfacial tension was found to increase with the aspect ratio (i.e., the ratio of diameters of molecular long and short axes) [88].

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. Here, $\theta=0^\circ$ and $\theta=90^\circ$ correspond to the homeotropic (or perpendicular) and planar (or parallel) anchoring, respectively. If the director does not orient with planar nor homeotropic anchoring, then the only stable anchoring is the oblique one [98]. The tilt angle depends upon the molecular symmetry rather than on the interactions type [96]. The surface anchoring also depends upon the aspect ratio of rod-like molecules [99,97]. Various iso-nm interfacial studies for different LC systems have found planar [73,96,75,100,93,95,79,76,86], homeotropic [97,100,101] and oblique [84,102,97,98] anchorings. The GB potential model (refer sec. 2.5.1 for details) with different set of GB parameters such as (κ , κ' , μ , ν) equal to (3, 5, 1, 3) [74] and (4.4, 20, 1, 1) [90] have resulted into the planar anchoring at the iso-nem interface (Fig. 1.5). Depending upon the type of surface anchoring, the surface tension can be different. The free energy cost is different for the interfacial fluctuations in the direction 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-nem interfacial tension (γ_{IN}) was found to be minimum at the planar anchoring [79,76,82,75,94]. However, in some studies, the minimum interfacial tension was found at the tilt angle of $\pi/3$ for rigid rods [84], and hard spherocylinders [97]. The biaxial effect on the iso-nem interface has also been well studied [94,81,73,79,76,98].

The interfacial anchoring can be modified by external magnetic or electric fields

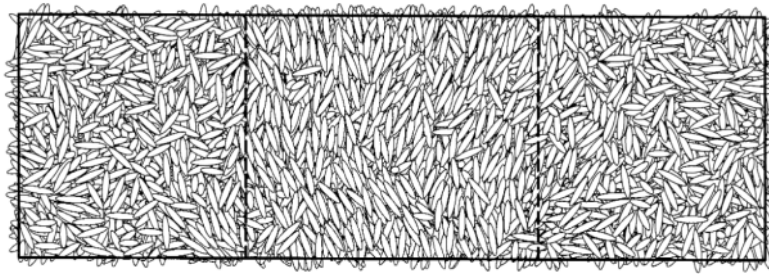


Figure 1.5: The isotropic-nematic interface, obtained by Martin A Bates, *Chem. Phys. Lett.* **288**, p. 209-215 (1998), in the case of GB liquid crystalline system [90].

and by adding certain contributions to the intermolecular potential [74]. The external magnetic or electric fields can manipulate the director alignment in some LC materials and tune their optical properties [76]. The shear flow can lead to material orientation, form new structures, shift the phase boundaries and thus enforce the ordering transitions [91]. The interfacial polar ordering can also influence the director for the tilt orientation [96]. In a study of hard rods, the tilted director resulted due to the opposing contributions by the perpendicular alignment on entropic grounds and the parallel alignment due to direct interaction between molecules of two phases [97]. The homeotropic anchoring can be induced by selecting special boundary conditions or by preparing the initial nematic slab configuration with the normal orientation [87]. Apart from the static iso-nem interface, the iso-nem interfacial tension for the dynamic interface has also been reported using the time-dependent Ginzburg-Landau theory [51]. Onsager suggested that the iso-nem interface is flat, i.e., there are no capillary-wave fluctuations at the interface. However, Onsager's assumption is only valid for infinitely elongated particles [89]. The fluctuations in ²² nematic liquid crystals have been well studied using the Ericksen-Leslie theory, Ginzburg-Landau-de Gennes in the static case, and Langevin equations for the dynamic fluctuations [103].

1.6 Fluctuating interface

The knowledge of the dynamic fluctuations in the orientational tensor is important to describe the nucleation rate for the nucleating nematic phase and determine the capillary waves spectrum [103]. The fluctuations present at the interface increase the interfacial area which cost free energy [89]. The capillary wave spectrum has been extensively studied in various iso-nem interfacial studies ([88][91][87], and refs. therein) and to estimate the iso-nem interfacial tension ([89][76], and refs. therein). The capillary waves lead to the broadening of the simulated density and nematic order parameter profiles which further result in the additional broadening when the average profile width is calculated by fixing the center of mass [88]. The elastic interactions due to the nematic phase influence the capillary-wave spectrum and give rise to long-range interactions between the interfaces [91]. The long-range interfacial fluctuations result in the long-range elastic distortions in the director field. In the iso-nem interface, the capillary waves are found to be anisotropic due to stronger fluctuations in the director's perpendicular direction than in the parallel [91][89]. The strong planar anchoring at the interface leads to the particles' orientations along the interface which indicates the bending elasticity or flexible director regime (Fig. 1.6(a)) [76]. On the other hand, the strong bending rigidity does not allow the particles to orient along the shape of 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, the anisotropic interfacial tension dominates and results in a stiff director field as observed in [76] (Fig. 1.6(b)). In the computer simulation studies of interfacial fluctuations with the periodic boundary conditions, two parallel interfaces are formed. Therefore, an elongated simulation box should be used to avoid interfacial interactions and to measure the interfacial properties precisely. Such a box configuration leads to a large separation between two interfaces, with the interface normal

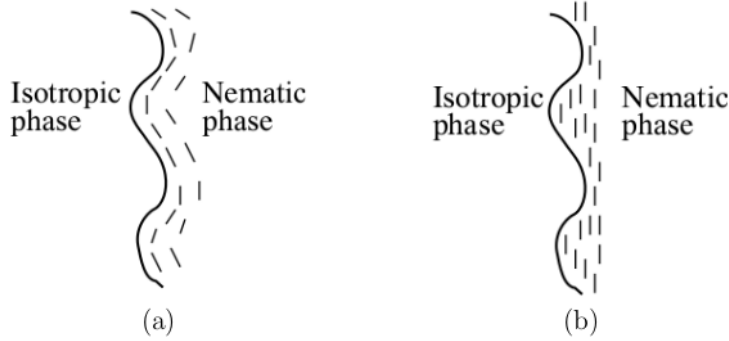


Figure 1.6: A sketch of the interfacial fluctuations or the capillary waves (adapted from the image shown by Wolfsheimer *et al.*, *Phys. Rev. E* **73**, p. 061703 (2006) [76]). The image (a) illustrates the strong interfacial anchoring in which the spectrum anisotropy is dominated by elasticity. The image (b) implies the strong bending rigidity in which the anisotropy of the interfacial tension influences the spectrum anisotropy

along the elongated dimension (to acquire the minimum interfacial area). However, the lateral dimensions might still have finite-size effects arising due to the ¹⁴capillary waves. Therefore, the lateral dimensions should also be large enough to determine the capillary spectrum with long-wavelength limiting form [88]. The capillary waves can also be observed in the isotropic-smectic interface, where there is a change in both ⁹positional and orientational order at the interface. The isotropic-smectic A (iso-smA) 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-smA interface [90].

1.7 Isotropic-Smectic A interface

For the iso-smA interface, a question arises whether the anchoring depends only upon the orientational correlations or the translational correlations ¹⁹also play a role in determining the anchoring. In a study done by M. A. Bates [90], the planar anchoring observed for iso-smA interfaces exhibited no influence of the translational order present in the smA phase on the average orientation at the interface. In this case, a narrow nematic layer between iso and smA phases was found due to

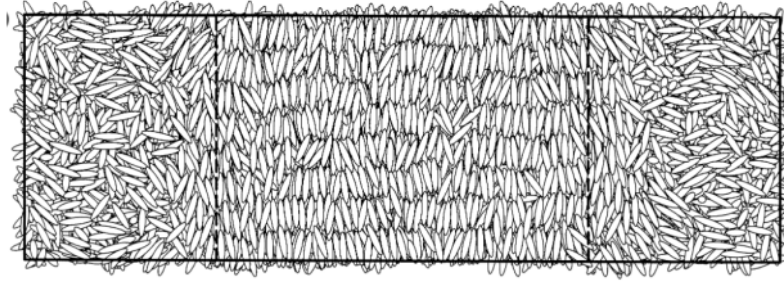


Figure 1.7: The isotropic-smectic interface, obtained by Martin A Bates, *Chem. Phys. Lett.* **288**, p. 209-215 (1998), in the case of GB liquid crystalline system [90]

the short-ranged orientational correlations, and no translational correlations in the isotropic phase [90]. The interfacial thickness, spatial varying orientational order, and the translational order near the iso-smA interface can be determined using the density and orientational order profiles [90]. The interfacial width of the iso-smA interface has been found to be larger than that of the iso-nem interface [90]. Thus, it is expected that the nematic-smectic A (nem-smA) interfacial width would be very large. Hence, very large systems would be needed to simulate the nm-smA interface [90]. Using MD simulations and GB potential model, the iso-smA interface has been studied with a set of GB parameters $(\kappa, \kappa', \mu, \nu)$ equal to (3, 5, 1, 3) [74], and (4.4, 20, 1, 1) [90]. The surface free energy of the interfaces between smA and isotropic [104], and smB [105] phases, has also been measured. Several growth patterns studies of smectic LCs from the isotropic phase showed that the shape of smA droplet depends on the interfacial tension anisotropy $\Delta\gamma = \gamma_{\parallel} - \gamma_{\perp}$ (subscripts signify the parallel and perpendicular directions to the smectic layer normal) [106]. The positive $\Delta\gamma$ indicates less interfacial tension along the smectic layers. As a result, during the nucleation process, smA droplets grew into an ellipsoidal shape with flat smectic layers normal to the ellipse's major 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 are also observed from the nematic phase [106]. However, 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].

Apart from the surface tension anisotropy, the droplets morphology is also found to be dependent on the anisotropy of kinetic effects [107].

1.8 Nematic-Smectic B interface

The thermotropic LCs consisting of rod-like molecules exhibit complex patterns during the phase transitions [107]. For the equilibrium-shape measurements, the smB phase is considered an appropriate choice due to rather fast transport [108]. Experimentally, the nucleation of the nematic phase in smectic-B 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 the quasi-two-dimensional geometry by bounding the LCs between the glass plates [108,107,109,111,110]. There, the equilibrium shapes of nm or 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) [108,107,109,111,56,112]. 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)) [108,107,109,111]. 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]. The smB germs in H (in H) configuration initially formed a circular shape which further goes 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], and during the smA-smB interface [115,104]. However, it is very rare to observe dendrites in rod-like thermotropic LCs [112]. In H

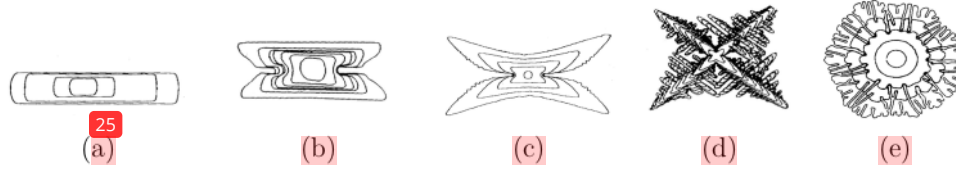


Figure 1.8: Different shapes of planar and homeotropic smectic-B germs in planar homeotropic nematic phase in a quasi-two-dimensional geometry. These images are taken from the work done by Buka *et al.*, *Phys. Rev. E* **51**, p. 571-578 (1995) [107]

(in P) configuration, an oval-shaped nem-smB interface was observed [111] with the long faceted sides connected to the short convex sides without any cusp in contrast to the smA-smB interface [104]. 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 [108,107,109,111]. Apart from the nm-smB fronts [116,117], the directional solidification has also been analyzed for smA-smB fronts [104,118]. In addition to the homogeneous nucleation, the liquid crystalline system undergoes several surface-ordering transitions when in contact with a surface [119]. Such surface-induced phase transitions or wetting phenomenon has attracted a lot of experimental and theoretical works.

1.9 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 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]. It is speculated that an oriented interfacial boundary layer or prewetting transition occurs for a particular surface interaction strength [124]. Depending upon the nature of surface interactions, the surface order parameter can be dependent or independent of temperature [124]. There are numerous studies on the pre-transitional surface alignment in isotropic and nematic LCs [125][126]. 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. It is expected that the bulk isotropic phase would have nematic-like surface order, and the bulk nematic phase would have smectic-like order. However, in the studies of the isotropic-air and nematic-air in-

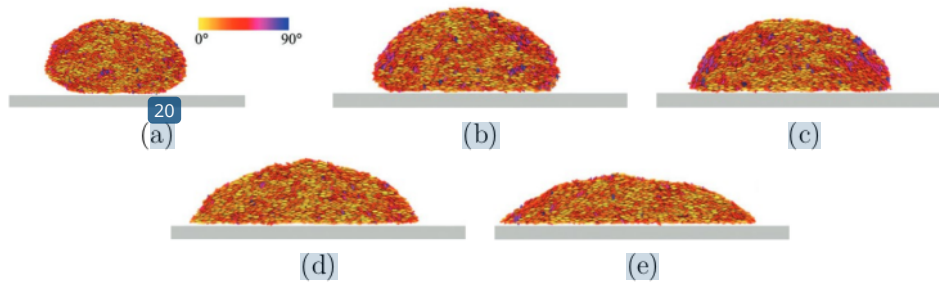


Figure 1.9: Wetting of the crystalline surface by equilibrated nematic nanodroplets from the vapor phase was observed by Vanzo *et al.*, *Soft Matter* **12**, p. 1610-1620 (2016) upon increasing affinity from (a) to (e). Vanzo *et al.* colored the particles differently to understand the tilt angle from the droplet director [127]. The image is taken from [127]

terfaces, the surface-induced smectic-like ordered phase was observed in both the cases [125]. These studies found discrete smectic layering with direct iso-smA phase transitions and continuous smectic layering with nem-smA transitions. Moreover, the free surface-induced smA phase in the isotropic phase was observed with the addition of single smectic layers near the surface through a series of discrete transitions [126]. These transitions are called layering transitions, similar to the first-order phase transitions found in multilayer solid adsorption [128]. Further, these layering

SECTION 1.9: WETTING PHENOMENON IN LCS

transitions are found to be significantly broader at the solid interface than the air interface [123]. Therefore due to the surface present, the isotropic or vapor phase often exhibit nematic or smectic order near the surface (Fig. 1.9) [127]. Furthermore, the effect of a glass plate on the nematic phase was found to be strongly attenuated due to the formation of a lamellar phase between them [129]. In this study, the main contribution to the surface energy was due to the interaction between the nematic and smectic layers. Further, upon cooling the nematic phase to the smectic-A phase, the smectic ordering was observed in a thin, planar-aligned liquid crystalline shell geometry [130]. Some studies on the smectic LCs found that the orientations of the surface and bulk molecules are very different [131, 132, 77, 133]. It might be due to the substantial effect of the undulations on bulk smectic LCs than on the surface smectic phase [128]. As a result, the free energy increased more in the 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 [124]. This result suggested a local interaction between the surface layer and the wall. Experimentally, the liquid crystalline orientational order at the surface has been measured using various techniques such as birefringence, evanescent-wave-ellipsometry, surface second-harmonic generation (SHG), field-induced twist, x-ray scattering, combined optical and capacitance measurements and deuterium *NMR* [124, 21]. For instance, using the surface birefringence and ellipsometry experiments, the surface-induced nematic order was observed as the system attained the bulk first-order isotropic-to-nematic transition temperature (T_{IN}) [134]. The surface-induced layering phenomena above isotropic-smectic and nematic-smectic phase transitions have also been investigated using various theoretical approaches [125, 135, 128]. The study of the confined liquid crystals, defined by the Lewbohl-Lasher Hamiltonian model, exhibited very weak first-order nematic and isotropic wetting transitions at large and weak surface fields, respectively [119]. 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]. Therefore, the knowledge of the surface anchoring

mechanism is important to determine the interaction of a liquid-crystalline material with the solid surface, and hence to understand the wetting phenomena.

1.10 Surface anchoring during wetting

Although, the anchoring of molecules at the interface formed between two phases in an unconfined liquid crystalline system is already discussed in earlier sections. Here, we have discussed about the anchoring behavior of LC molecules near a surface during wetting. The molecular alignment in LCs confined by a surface is essential to the fundamental issues in physics and biology. The possible alignments of LCs on the surface are planar, homeotropic, and tilted, as shown in Fig. 1.10. Various theoretical approaches such as Landa-de Gennes, Maier-Saupe, and molecular methods⁴¹ have been used to determine the orientational ordering of LCs near the surface¹²⁴. The alignment near the surface is influenced by several factors²⁰ such as the type of the coating material, the type of liquid crystal used, the method used to coat the substance, and the technique used to orient the surface material¹²⁵. For instance, the surface roughness has a pronounced effect on the angular distribution functions of the particles near the surface⁹¹³⁷. There is a well understanding of

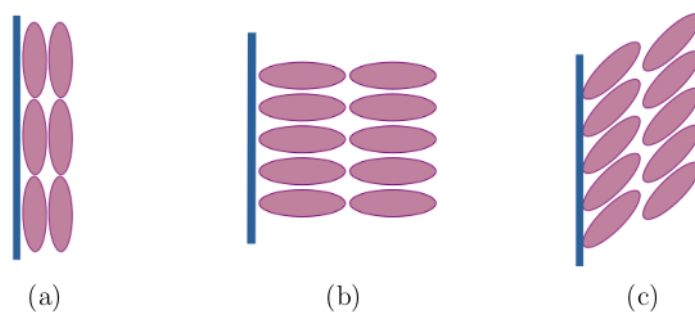


Figure 1.10: A pictorial representation of liquid crystalline particles on the surface with (a) parallel, (b) homeotropic, and (c) oblique anchoring

the molecular features affecting the anchoring of the nematic phase in the vicinity of solid and free interfaces⁷¹¹³⁸¹²⁹. In the presence of a solid untreated surface, the excluded volume effect and van der Waals attractions of the surface

induced a random planar alignment among the surface molecules [119]. Both the parallel and perpendicularly aligned surface-induced nematic phase have been observed for the bulk isotropic phase with different surface treatments [124]. At the cleaved graphite surfaces, the LC molecules were arranged in an ordered array with their alignments in the plane of surface [123]. Various experimental studies have observed the surface-induced layers parallel to the surface with tilted or homeotropically aligned molecules [71]. Homeotropic anchoring is essential in appliances using vertically or hybrid aligned nematic cells [125]. The surfactants, such as ¹⁰⁴sodium dodecyl benzene sulfonate (SDBS, LAS) or sodium dodecyl sulfonate (SDS), can induce the homeotropic anchoring [139]. The homeotropically aligned smectic layers at a silicon surface (treated in different ways) was observed in a nematic LC [125] and with a direct iso-smA transition [126][123]. 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]. Furthermore, there are various studies that investigated the molecular alignment at the LC-air interface for nematic and smectic LCs ([131], and refs. therein). At the LC-air interface, the nematic exhibited two smectic layers, and the smectic showed multiple distinct surface layers with the homeotropic anchoring [131].

1.11 Complete or incomplete wetting

For confined systems, the liquid crystalline droplets of different shapes can be found depending upon the surface anchoring conditions [140], and the elastic constants of LCs [141]. Further, depending upon the droplet's interaction with the surface, a surface can be completely or incompletely wetted by the droplet (Fig. 1.11) [142]. Earlier theories suggested that if the nematic-smectic A (nm-smA) is a first-order transition, the surface exhibits discrete smectic layers with incomplete wetting. Otherwise, if ²it is a second-order transition, then the continuous smectic layering is observed with complete wetting [125]. An experimental study showed that the

complete or incomplete surface wetting by smA depends upon the strength of the surface interaction potential [125]. The complete or incomplete wetting by the nematic phase is found to be dependent upon the surface ordering field, and a surface pre-wetting transition may occur before the complete wetting. For the complete wetting [27] there should be a logarithmic divergence of an integrated order parameter $\Gamma = \int_0^\infty Q(z)dz$ as $T \rightarrow T_{IN}$ [128]. Telo da Gama has expressed the free energy in terms of the one-particle density distribution function and observed the complete wetting of the surface by the nematic phase [143].

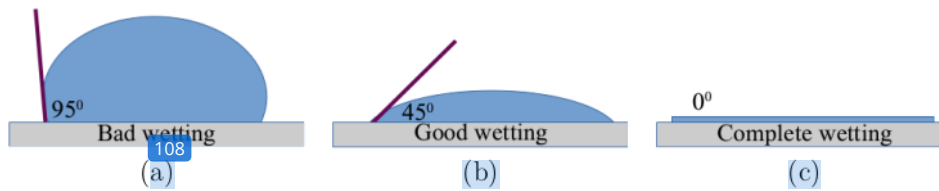


Figure 1.11: The pictorial illustration of the wetting behavior of droplets on the surface with the contact angle of (a) 95° for bad, (b) 45° for good, and (c) 0° for complete wetting (adapted from [142])

By using Monte Carlo simulations and mean-field theoretical calculations, Luckhurst *et al.* [144], and Pawlowska *et al.* [135] also found the complete wetting by the nematic phase at an extremely high surface field. To understand the smectic wetting, Pawlowska *et al.* [135] developed a lattice model based upon the Ronis and Rosenblatt work [145, 146]. However, this model showed 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. Another limitation was the inappropriate layering description that could not exhibit the physics of a real continuum system [128]. With the literature review presented above, it has been found that there are some gaps available in the nucleation studies of liquid crystalline material such as in nematic-smectic B interface, the calculation of interfacial tension of confined LCs. In view of this, we have provided the motivation, in the next section, leading to the objectives of this thesis.

1.12 Motivation of the thesis

The homogeneous nucleation and wetting phenomena have been extensively studied in materials composed of spherical particles. The interfacial properties of different interfaces, such as liquid-vapor, solid-fluid, solid-surface, and fluid-surface interfaces, have been determined using various model systems for the spherical particles. However, in reality, the particles of the molecular materials are not only spherical. Hence, there is a need to study a system containing anisotropic particles, such as a liquid crystalline system. Due to the complex and sensitive phase diagram of LCs, the interfacial phenomenon in LC material leads to interesting interfacial properties. For instance, the variation in the orientational order of molecules near the isotropic-nematic interface has numerous applications in functional materials, biosensors, etc. Therefore, there are an enormous amount of studies on determining the interfacial properties of isotropic-nematic interfaces, including the nematic-vapor and isotropic-vapor interfaces. Several works have also analyzed the morphology of isotropic or nematic droplets formed during the iso-nem coexistence. However, the interfacial studies are inadequate for the nematic-smectic B interface.

A precise knowledge of interfacial phenomena in LCs, including the nm and smB phases, is required to develop better LC material using suitable processing methodologies. Thus, there arises a need to determine the interfacial properties of the nm-smB interface and scrutinize the nm-smB phase coexistence. It is also important to note that such studies are an important endeavor because accurate estimation of interfacial properties is indispensable for applications in crystal nucleation and growth phenomena. In a quasi-two-dimensional geometry, the nm-smB coexistence has been well studied, resulting in different shapes of nucleating nm and smB droplets (as discussed earlier). However, as far as we know, the morphologies of homogeneously nucleated nm and smB droplets within the nm-smB coexistence has not been studied in a 3D system to date. Moreover, the study of the wetting behavior of an LC material confined by a surface is indispensable for various technological purposes, such as liquid crystal displays. Therefore, the behavior of an

LC material in the vicinity of several surface potentials has been analyzed in various studies. However, ¹¹³ to the best of our knowledge, the interfacial tension of an LC material confined by soft, smooth, and repulsive walls has not been calculated yet. 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 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.

As the experimental observation of the rare nucleation event is challenging, then the computer simulations prove beneficial to understand the nucleation phenomenon. Therefore to accomplish the thesis objectives, the simulations are performed by using LAMMPS package that uses the MD simulations technique. The interaction between liquid crystalline particles is defined by using a Gay-Berne potential model. In the next chapter, we will discuss the nucleation phenomenon in detail, the liquid crystalline model, the computational technique used, and the methods we 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) [28]. The validity of CNT was doubted in various studies. The most significant controversy arose when Lothe and Pound suggested that the nucleating clusters should be considered large molecules. Their translational and rotational partition functions should be included along with the free energy contributions from CNT so that the droplet translates and rotates much more freely than the corresponding volume in (bulk) liquid. As a result, the nucleation rate increased by factors ranging from 10^{14} to 10^{20} . Then, Reiss *et al.* found that the Lothe-Pound treatment was incorrect because it double counted certain free energy contributions. With their corrections, they obtained a result close to CNT again, which was later counterargued by Lothe and Pound emphasizing the accuracy of their treatment [28]. The CNT yields a basic but elegant description of the nucleation, specifically the homogeneous nucleation (Fig. 2.1(a)). It is based on the unimolecular reaction kinetics and equilibrium statistical mechanics. The CNT depicts that the work is required to form a droplet, and the droplet free energy can be written in terms of the droplet's volume and surface free energies [10]. For this nucleation event to take place, there

is a need ⁸ to overcome a free-energy barrier that comprises the competition between the surface and bulk-free energies (Fig. 2.1(b)). In other words, CNT states that a single nucleating droplet of the new stable phase expands by adding the single molecules in a sea of the metastable mother phase. The size of this droplet must be greater than the critical size (r^*) to compensate 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 upon the capillarity approximation, the CNT treats the small clusters of the nucleating phase as the macroscopic regions of space. CNT assumes that the droplet's ² surface free energy is equivalent ¹² 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 cluster (or droplet) can be written as ¹⁷

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

The first one is the surface contribution term (F_S), with γ being the interfacial

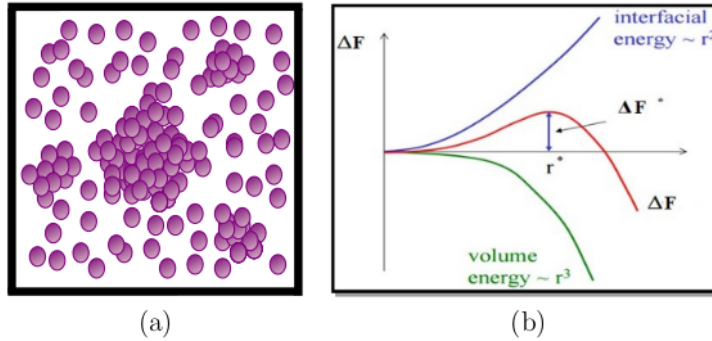


Figure 2.1: (a) A cartoon image shows the homogeneous nucleation phenomenon in a system with periodic boundary conditions (without any wall). (b) The variation of surface, volume, and total free energy associated with the homogeneous nucleation is shown, where r is cluster radius

tension, and ⁸² A is the cluster's surface area. The second term (F_V) is the free energy difference between the bulk cluster 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

SECTION 2.1: HOMOGENEOUS AND HETEROGENEOUS NUCLEATION

energies per unit volume, and V is the cluster volume. Here, $\Delta\mu = \mu - \mu_{coex}$ is the chemical potential difference relative to the coexistence value, and ρ_1 and ρ_2 are the bulk densities of the nucleating and the mother phases, respectively. The free energy per unit volume of the thermodynamically stable new phase is lower 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. Therefore, in most cases, the spherical critical nucleus of radius r is formed with $A=4\pi r^2$ and $V=(4/3)\pi r^3$. As a result, the free energy required for the formation of a spherical droplet or cluster becomes [3]

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

where ΔF_{hom} depends upon r or the cluster size $n=\rho_{cl}V$, which is the number of molecules constituting the cluster. Here, ρ_d is the number density of the bulk cluster. The maximum value of ΔF_{hom} is ΔF_{hom}^* at $n=n^*$ which represents the thermodynamically defined critical cluster with the barrier height of $16\pi\gamma^3/3|\Delta f_V|^2$ [8]. The barrier height strongly depends on the 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 [3]

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

Here, the subscript s in the surface free energy term ($F_s(r^*)$) indicates the spherical shape of the droplet. Hence, Eq. 2.3 implies that the nucleation barrier can be obtained directly by using the surface free energy of the spherical nucleating droplet. The free energy barrier (ΔF_{hom}^*) required for the spontaneous emergence of a critical nucleus of a nucleating (new) phase in the bulk is of the order of $20 k_B T \geq \Delta F_{hom}^* \leq 200 k_B T$. Hence, nucleation is a rare event compared to the thermal fluctuations that can easily be detected using scattering experiments. In the case of heterogeneous nucleation, a macroscopic droplet nucleates from the mother phase on a surface

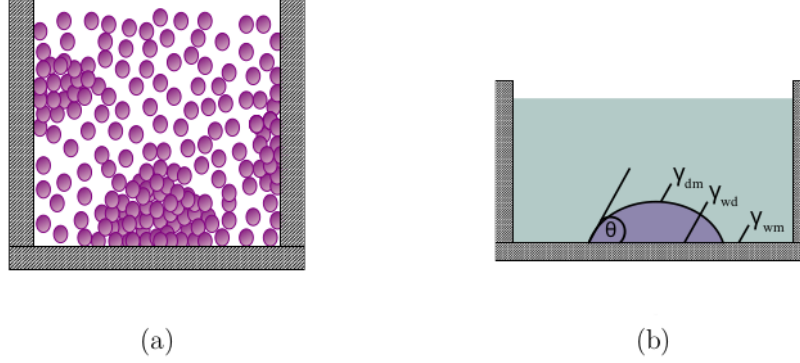


Figure 2.2: (a) A cartoon image shows the heterogeneous nucleation phenomenon with the formation of droplets on the walls of an open container. (b) A reference image illustrates the contact angle (θ) and three interfacial tensions (γ_{wd} , γ_{dm} , and γ_{wm}) defined in Young's equation for a spherical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

or walls of a container (Fig. 2.2(a)). For the heterogeneous nucleation theory, the Turnbull's equation [147] is considered as a keystone. In 1895, Thomas Young formulated an equation to understand the heterogeneous nucleation and named it as the Young's equation [148]. This equation was further generalized by adding a line-tension term due to three-phase contact line [149] which further modified the conventional heterogeneous nucleation theory [150, 151]. Then, the dependency of line-tension on the transition order [152], radius of spherical droplet, contact angle between two phases and contact-line radius [153] was found. Young's equation describes the shape and behavior of a droplet where the droplet-mother interface meets the surface (Fig. 2.2(b)), and is given by [3]

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

where θ is the contact angle between the droplet and the wall and can be determined by knowing the three competing interfacial tensions due to the droplet-mother (γ_{dm}), wall-droplet (γ_{wd}), and wall-mother (γ_{wm}) interfaces (Fig. 2.2(b)). The contact angle (θ) determines the wetting behavior of the nucleus. For example, $\theta = 0^\circ$ indicates the complete wetting with the layering structure of the droplet, $\theta = 90^\circ$ results in

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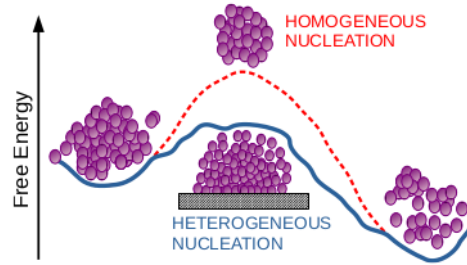
the bad wetting, and $\theta = 180^\circ$ implies the homogeneous nucleation of a droplet without wetting the walls or surface. By considering the geometry of the droplet as a spherical cap (as per the CNT assumptions), the Turnbull's surface free energy [3] is given by

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

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

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

This Eq. [2.6] implies that for the [3] heterogeneous nucleation, the free energy barrier is decreased (Fig. [2.3]) by a Turnbull's factor of $f(\theta)$.



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

Furthermore, CNT suggested that the material at the core of the nucleus is a new [8] bulk phase and the surface free energy of a small nucleus [75] 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. Also, this theory is not appropriate at a very large supersaturation ratio, leading to the critical nucleus's small size and very large nucleation rate. Several studies found a discrepancy between the results obtained from this theory and nucleation experiments [6]. For the small liquid droplets coexisting in bulk vapor, Tolman took the first step apart from the capillarity approximation, and proposed the phenomenological [39] Tolman length (δ)

to express the curvature dependent surface tension $\gamma(r) = \gamma_{vl}/(1 + 2\delta/r)$ (where γ_{vl} is the liquid-vapor interfacial tension) [10]. However, the precise definition of δ was difficult in the context of statistical mechanics. Then based upon Fischer's droplet model, the logarithmic corrections in the free energy equation were made [10]. On the molecular scale, the vapor-liquid interface is diffuse rather than sharp. Therefore, the nucleation free energy (ΔF) can not be separated into bulk and interfacial terms [10]. These theoretical gaps result in an inadequate understanding of homogeneous nucleation. Moreover, using experiments, the homogeneous nucleation study of liquid droplets in supersaturated vapors is challenging because: (i) the size and density of critical droplets are so small that it is impossible to observe them directly. These droplets can only be detected by using light scattering methods [10] if they grow to a size much greater than the critical size. (ii) The heterogeneous nucleation at any nucleation site must be avoided carefully because the nucleation agents may dramatically decrease the free energy barrier. Therefore, even a tiny amount of these agents may manipulate the measurements [10]. 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 [65]. The nucleation rate is extremely sensitive to experimental conditions such as temperature, pressure, impurity concentrations, etc., because of its exponential dependence on the rapidly changing free energies. Consequently, it makes reproducing the experimental data difficult and leads to large uncertainties in the theoretical estimation of nucleation rate. In contrast, the simulations play a crucial role in filling the gap between the experiment and theory. Hence, the simulations have been successfully used in various nucleation studies [3]. The use of periodic boundary conditions helps to avoid the walls, and no other impurities occur during simulations. Moreover, the simulations provide complete information about the atoms' positional coordinates, which makes the measurements possible at the nanoscale or single atomic scale. For the efficient study of the nucleation phenomenon using computer simulations, large systems need to be simulated for a very long time because nucleation is a rare event for $\Delta F \gg k_B T$.

2.2 Molecular dynamics simulations technique

We have used the Molecular Dynamics (MD) simulations technique to perform the computer simulations. MD technique is a computational approach that is used to compute the static and dynamic properties of a classical system such as pressure, diffusion coefficient etc. [154, 155, 156, 157, 158]. The measurable quantity, in MD technique, should be expressible in terms of positions and momenta of particles. Conventionally, the total energy is conserved in MD, and thus the microcanonical ensemble (NVE) can be used for the simulations. MD technique is advantageous over the Monte Carlo (MC) simulations technique because the static and dynamic properties of the system can be studied with MD. However, the MC technique can only study the static properties of the system. MD is a better option if the system weakly depends on temperature than the other interactions strength. Moreover, the results from the experiments and MD simulations are comparable. The MD technique includes three steps to simulate a system [159]: Initialization, force calculation, and integration of Newton's equations of motion.

1. Initialization: Firstly, the system is initialized in which the initial system and per-atom properties are defined. The system or global properties include the temperature, time step, density, etc. The per-atom properties include the 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 shifted 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. Therefore, for the force calculation in a system containing N particles with pairwise additive interactions, the $N(N - 1)/2$ pair distances are evaluated.

In this step, the force calculations are done 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 the Newton's second equation of motion. There are various MD algorithms to perform the calculations. One of them is the Verlet algorithm in which the updated particles' coordinate and velocity at time step $t + \delta t$, using Taylor's expansion and by ignoring the higher powers, can be computed as

$$\mathbf{r}(t + \delta t) \approx 2 \mathbf{r}(t) - \mathbf{r}(t - \delta t) + \frac{f(t)}{m} \delta t^2, \quad (2.7)$$

$$\mathbf{v}(t) = \frac{\mathbf{r}(t + \delta t) - \mathbf{r}(t - \delta t)}{2\delta t}. \quad (2.8)$$

Here, δt is the time step size. Using the velocity expression, the instantaneous kinetic energy, and then the instantaneous temperature can be calculated as

$$T(t) = \frac{\sum_{i=1}^{\infty} m_i v_i^2(t)}{k_B N_f} \quad (2.9)$$

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 (m) are taken as unity. To calculate the particles' positions at further time steps, 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 time step. This algorithm is fast, area-preserving, time-reversible, and needs little memory but is not accurate for long time steps.

2.2.1 Other MD algorithms

In addition to the Verlet algorithm, there are other various MD algorithms to update the positions and velocities [156] such as Euler, Leap Frog [159], Velocity Verlet [160], Beeman [159] and velocity-corrected Verlet [159] algorithms. According to the Euler

algorithm, the updated positions can be calculated ¹as

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

The Euler algorithm is irreversible, includes energy fluctuations, and not area preserving. Using the ²⁸Leap Frog algorithm ¹⁵⁹, the positions and velocities are computed at half of time steps as

$$\mathbf{v}(t - \delta t/2) \equiv \frac{\mathbf{r}(t) - \mathbf{r}(t - \delta t)}{\delta t}, \quad \mathbf{v}(t + \delta t/2) \equiv \frac{\mathbf{r}(t + \delta t) - \mathbf{r}(t)}{\delta t}. \quad (2.11)$$

Then, new ³⁰positions can be found as

$$\mathbf{r}(t + \delta t) = \mathbf{r}(t) + \delta t \mathbf{v}(t + \delta t/2). \quad (2.12)$$

This algorithm is not suitable for computing the total energy because the positions and velocities are calculated at different times (i.e., positions ¹at $t + \delta t$ and velocity at $t + \delta t/2$). According to ³⁸the velocity verlet algorithm ¹⁶⁰,

$$\mathbf{r}(t + \delta t) = \mathbf{r}(t) + \mathbf{v}(t)\delta t + \frac{\mathbf{f}(t)}{2m}\delta t^2, \quad \mathbf{v}(t + \delta t) = \mathbf{v}(t) + \frac{\mathbf{f}(t + \delta t) + \mathbf{f}(t)}{2m}\delta t. \quad (2.13)$$

There is one more Verlet-like algorithm, i.e., the Beeman algorithm ¹⁵⁹ which gives the identical trajectories. However, it is time irreversible and provides more accurate velocities than the Verlet algorithm. The problem of time irreversibility can be resolved by using a velocity-corrected Verlet algorithm ¹⁵⁹. In addition to the NVE ensemble, the MD simulations can also be performed with a canonical ensemble (i.e., NPT or NVT) ¹⁶¹¹⁶² by using some temperature ¹⁶³ and pressure control methods.

2.2.2 MD at constant temperature

For the canonical (NPT or NVT) MD simulations, there are various methods to control the temperature:

-
1. Velocity scaling: The desired temperature ⁹ can be achieved by rescaling the randomly chosen initial velocities by using a thermostat known as the isokinetic and berendsen thermostat [164]. The isokinetic thermostat keeps the kinetic energy constant and ¹ can be used only during initialization but not to simulate a canonical ensemble. ¹ To achieve a desired temperature T , the velocities are scaled by

$$\frac{3}{2}Nk_B T = \frac{1}{2} \sum_i m_i v_i^2, \quad \lambda = \sqrt{(T/T_i)}. \quad (2.14)$$

In the Berendsen thermostat [164], the velocity scaling is done by using a scaling factor of

$$\lambda = \left[1 + \frac{\delta t}{\tau_T} \left(\frac{T}{T_0} - 1 \right) \right]^{\frac{1}{2}}. \quad (2.15)$$

²⁴ where t is the time step, T_0 is the target temperature, and τ_T is temperature rise. The Berendsen method is not recommended because it slightly deviates from the canonical ensemble.

2. Stochastic thermostats (NVT): There are three stochastic thermostats, such as the Anderson, Langevin, and Dissipative Particle Dynamics (DPD). The easiest and correct method to simulate an NVT ensemble is the Anderson thermostat [163]. In Anderson thermostat, the probability of assigning the chosen particle's velocity at temperature T is

$$P(\rho) = \left(\frac{\beta}{2\pi m} \right)^{3/2} \exp \left[-\beta p^2 / (2m) \right] \quad (2.16)$$

The Langevin thermostat includes the stochastic forces and the constant friction which reduce the particles' velocities [165]. The diffusion coefficients can not be evaluated using the Anderson and Langevin thermostats. The DPD thermostat [166] can be used to evaluate the transport properties. It includes the addition of pairwise stochastic and dissipative forces to the particles. The momentum transport is conserved in DPD.

3. Nose-Hoover thermostat: Nose-Hoover is the most effective thermostat obtained by Nose and Hoover [167][168][169][170]. It includes extensive Lagrangian formalism, and no stochastic forces or velocities are calculated in this thermostat.

Like thermostats, there are several barostats [171] in which the desired pressure is maintained by controlling the system volume.

2.2.3 MD at constant pressure

In a system, the pressure² can be maintained by using different methods: (a) The instantaneous pressure can be made equal to the desired pressure by periodically rescaling the system volume. (b) The Berendsen barostat [164] can be used to periodically rescale the system volume²⁵ by a weak coupling between the system pressure and pressure bath. (c) In the Andersen barostat, the coupling of the system with an imaginary pressure bath is done with the addition of new degrees of freedom and use of an extended Lagrangian approach. To accomplish our thesis objectives, the simulations are performed by using a LAMMPS package that uses the classical MD technique. The MD simulations are run with the canonical ensemble by using the Nose-Hoover thermostats in LAMMPS.

2.3 LAMMPS

Originally developed at Sandia National Laboratories U.S., LAMMPS is a¹⁶ Large-scale Atomic/Molecular Massively Parallel Simulator package [172][173]. It is an open-source code available under GNU Public License Version 2 (GPLv2). LAMMPS currently contains source codes¹³ written in C++, but the earlier versions were written 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 includes both the short and long-range interaction models. It 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 in which the quantities are made unitless by reducing them with the Lennard-Jones parameters (i.e., σ and ϵ). The results obtained with such a 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 by 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 dimensionality of the system is fixed by the `dimension` command. The periodic or `non-periodic` (fixed or shrink-wrapped) boundary conditions of the box in three dimensions (x , y , and z) can be defined by `boundary` command. The next thing 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 the case of `lj`

units. Different keywords can also be defined to construct 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

```
13create_box      N region-ID keyword value
```

where `N` is the number of atoms types, `region-ID` is the region name and other optional keywords. There are various commands to define different properties of a particle, such as style, shape, size, mass, velocity, etc. Firstly, 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 atom with their mass, size, and random orientations defined by the `set` commands. The velocities can be assigned to these particles by using

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

where style can be `create`, `set`, `scale`, etc., with their arguments defined. Further, the interaction between particles is defined by a ¹³`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 for our system with arguments of γ (shift for potential minimum), ν , μ , and cut-off value parameters defined in GB potential (described later in detail). Further, 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 by using a `package gpu` command at the top of the script. 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, ²⁵ `time step size` during `the` run, etc. `The time step` command can specify `the` time step size for 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, and so on. The `compute` command is written as

`compute` ¹¹ `compute-ID group-ID style arguments`

where `compute-ID` is a `user-assigned name`, `group-ID` is `the group` of atoms included for the computation, and `style` can be any of the `property/atom`, temperature (`temp`), extra degrees of freedom (`extra/dof`), etc. with their arguments specified. Now, in order to fix the ensemble to be used, update the atoms' positions and velocities, enforce boundary conditions, etc., 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`, and so on, with arguments defined for that particular style. In our simulations, we have used `npt/asphere` and `nvt/asphere` fix styles which uses Nose-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 time steps. For this, the `run` command is

used as

```
run                N keyword values
```

where N is the number of time steps. Other keywords with their values can also be mentioned. Moreover, the current state of the simulation can be stored in binary files in every N time steps by using a `restart` command as

```
restart            N file1 file2
```

If one file name is specified (i.e., only `file1`), a series of filenames, including the time step, is created. However, the specification of two filenames creates only two files (i.e., `file1` and `file2`), and LAMMPS toggles between them during successively writing the restart files. Using restart files, we can continue the simulations from the same point where the previous run ends by 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 log files using the command

```
thermo.style      style arguments
```

with various styles. 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. With a `thermo` command, the time steps after which the quantities will be written in a log file or screen can be defined. Now, the instantaneous per-atom properties such as their positions, orientations, etc. can be printed in dump files by using the `dump` command as

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

Here, the style has a long list of options available. With the `custom` style, we can print the required quantities, such as positions (i.e., `x`, `y`, and `z`) and quaternions (i.e., `c-q[0]`, `c-q[1]`, `c-q[2]`, and `c-q[3]`), after every N time steps. 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>). Using the LAMMPS

package, we have simulated 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 with intermediate properties between a liquid and a crystal. Therefore, these phases are called liquid crystals (LCs) [36, 41, 174]. The liquid crystalline material is comprised of rod-like (elongated) [175] and disc-like shaped molecules. In LCs, the phase transition depends on several factors due to which the LCs are categorised into different types. The types of LCs are 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 [176]. Metallotropic LCs are composed of organic and inorganic molecules, and undergo phase transitions when the organic-inorganic composition ratio, concentration, and temperature are varied. Thermotropic LCs consist of organic molecules and undergo phase transitions upon varying the temperature [41]. Apart from the isotropic, nematic, and smectic phases (shown earlier in Fig. 1.2), the thermotropic LCs also exhibit cholesteric and columnar phases. The cholesteric phase, which is like the nematic phase, includes a differently aligned director in a regular fashion right through the medium. The columnar phase [177] is made up of disc-like (discotic) molecules which are singled-dimensionally stacked to form cylindrical structures. LCs are present everywhere in nature such as in 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 [178] 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 successfully used to study thermotropic LCs using various model systems [179]. Most of the computer simulations of thermotropic

LCs [92, 38, 39, 180, 40, 181, 182, 174, 183] have used the Gay-Berne (GB) [92] pair potential model, which is an anisotropic version of spherical Lennard-Jones (LJ) (6-12) [184] potential.

2.5 Interaction potential models

2.5.1 Gay-Berne potential model

The liquid crystalline system has been studied using various approaches such as the Onsager model, Maier and Saupe theory, discrete-orientation models, lattice theories, scaled-particle descriptions of nematic, and density functional theory [96]. However, the Gay-Berne (GB) potential [92] is found to be the most successful interaction potential to simulate the aspherical particles [38, 185, 186]. The GB potential depends on the intermolecular separation as well as the molecular orientations (Fig. 2.4(a)). The GB model considers the molecules of LC material as ellipsoids of revolution having a single-site representation in terms of the positions of their centers of masses. 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

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

$$\text{where, } R = \frac{r_{ij} - \sigma(\hat{\mathbf{r}}_{ij}, \hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j) + \sigma_0}{\sigma_0} \quad (2.17)$$

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

$$\sigma(\hat{\mathbf{r}}_{ij}, \hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j) = \sigma_0 \left[1 - \frac{\chi}{2} \left\{ \frac{\{(\hat{\mathbf{u}}_i + \hat{\mathbf{u}}_j) \cdot \hat{\mathbf{r}}_{ij}\}^2}{1 + \chi(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j)} + \frac{\{(\hat{\mathbf{u}}_i - \hat{\mathbf{u}}_j) \cdot \hat{\mathbf{r}}_{ij}\}^2}{1 - \chi(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j)} \right\} \right]^{-\frac{1}{2}} \quad (2.18)$$

with $\chi = (\kappa^2 - 1)/(\kappa^2 + 1)$. Here, the aspect ratio κ , is a measure of the ratio of the molecular diameters along major axis (σ_{ee}) to minor axis ($\sigma_{ss} = \sigma_0$). 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

$$\epsilon(\hat{\mathbf{r}}_{ij}, \hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j) = \epsilon_0 [\epsilon_1(\hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j)]^\nu [\epsilon_2(\hat{\mathbf{r}}_{ij}, \hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j)]^\mu, \quad (2.19)$$

$$\epsilon_1(\hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j) = [1 - \chi^2(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j)^2]^{-1/2}, \quad (2.20)$$

$$\epsilon_2(\hat{\mathbf{r}}_{ij}, \hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j) = 1 - \frac{\chi'}{2} \left[\frac{\{(\hat{\mathbf{u}}_i + \hat{\mathbf{u}}_j) \cdot \hat{\mathbf{r}}_{ij}\}^2}{1 + \chi'(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j)} + \frac{\{(\hat{\mathbf{u}}_i - \hat{\mathbf{u}}_j) \cdot \hat{\mathbf{r}}_{ij}\}^2}{1 - \chi'(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j)} \right] \quad (2.21)$$

with $\chi' = (\kappa^{1/\mu} - 1) / (\kappa^{1/\mu} + 1)$ 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 end-to-end (ϵ_{ee}). This parameter influences the formation of a smectic phase. The exponents μ and ν are the adjustable parameters which 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 [187]. The set of these four parameters ($\kappa, \kappa', \mu, \nu$) characterizes each member of a family of GB potential model. 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 can be prolate (rod-like if $\kappa > 1$) or oblate (disc-like if $\kappa < 1$) molecules. As most of the real mesogens are rod-like [189] whose constituent molecules must have an aspect ratio equal to or greater than 3 : 1 [187]. Therefore, we have chosen ellipsoids of a 3 : 1 aspect ratio, which are comparatively easier to simulate than ellipsoids of a higher aspect ratio. Now, 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 set of GB parameters [190, 191, 186, 37, 187].

SECTION 2.5: INTERACTION POTENTIAL MODELS

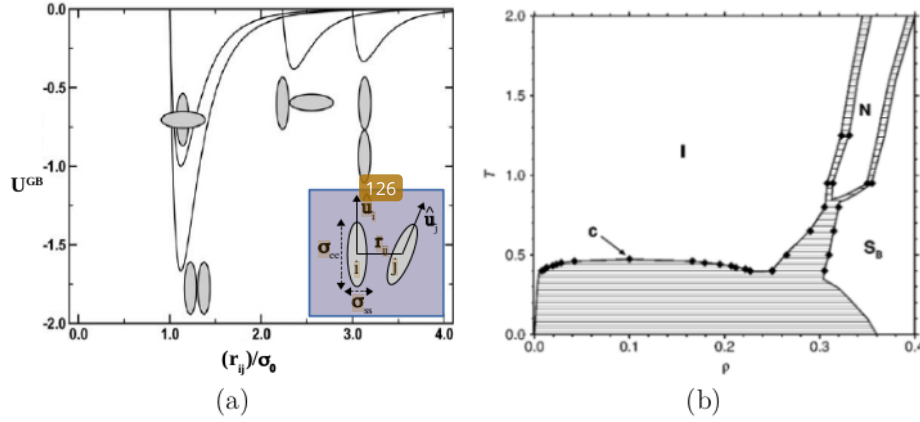


Figure 2.4: (a) The Gay-Berne²⁶ interaction potential between molecules orienting in different configurations, i.e., side-by-side, end-to-end, t-shaped, and crosswise. The image is taken from the work done by Razo *et al.*⁸ *Soft Matter*, **7**, p. 6828¹⁸⁸. (b) The Gay-Berne phase diagram exhibiting 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)¹⁷⁴

Here, we have used the (3, 5, 2, 1) set of GB parameters which have been extensively studied using computer simulations^{37,35,174,192,39,40,193} and theoretical approaches^{194,195}¹¹¹. The cut-off radius of the GB interaction potential is taken to be $4\sigma_0$. In the reported phase diagram for GB LCs, these parameters resulted into a rich phase diagram with a clear identification of isotropic, nematic, and smectic-B phases¹³⁴ (Fig. 2.4(b))¹⁷⁴³. As a result, there is a possibility of isotropic-nematic, isotropic-smectic B, and nematic-smectic B coexistence. Other GB potential parameters have also been studied, yielding other phases such as smectic-A, smectic-C, columnar, cholesteric, etc^{190,191,186,37,187}. All the thermodynamic quantities considered in our work are taken dimensionless in terms of molecular units of length⁸ 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 by using the typical values of molecular units. For example, $\sigma_0 = 5 \times 10^{-10}m$ (8CB mesogen's width¹⁹⁶), $\epsilon_0 = 1.4 \times 10^{-21}J$ (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 [127]. 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 [197,198] potential.

2.5.2 Weeks-Chandler-Anderson potential

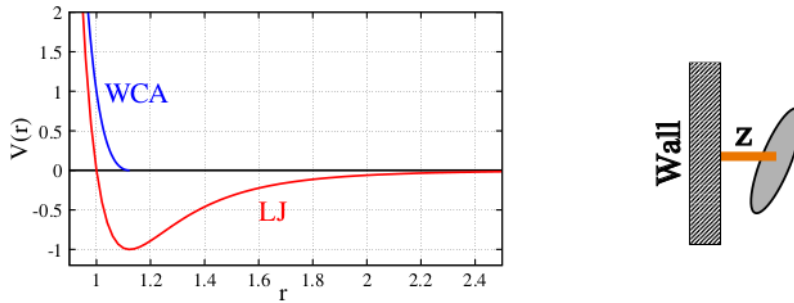


Figure 2.5: The soft, smooth, and repulsive Weeks-Chandler-Anderson (WCA) interaction potential between a wall and a particle.

The 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

$$\begin{aligned} V_{WCA}(z) &= 4\epsilon_W \left[(\sigma_W/z)^{12} - (\sigma_W/z)^6 + \frac{1}{4} \right] & 0 \leq z \leq \sigma_W 2^{1/6}, \\ &= 0 & \text{otherwise.} \end{aligned} \quad (2.22)$$

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 [199], investigate the behavior of the confined soft-repulsive nanorings [200], the interfacial properties of confined hard spheres [201], and colloid-polymer mixtures [202]. The main aim of our present thesis is to compute the interfacial properties of an interface between different phases of GB liquid crystalline material with and without confinement. For

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this, we have used Capillary Wave Theory and Pressure-Tensor methods to compute the interfacial properties of an interface formed in an unconfined and confined GB system, respectively, which are described below.

2.6 Computation of the interfacial properties

2.6.1 Capillary wave theory (CWT)

The surface free energy or surface tension is an extensive ³ quantity to define the properties of a surface. Therefore, its determination is significant in the statistical thermodynamical treatment of surfaces [203]. In 1894, the classic Van der Waals theory [204] 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 [205,206,207,208,209,210,211,212,203]. In a system with finite size and at finite temperature, the interface, where the particles of two different phases coexist, is never sharply defined. The particles near the interface constantly find their surroundings change due to the thermal fluctuations, leading to interfacial undulations. 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 [213,214]. In soft matters, 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. The capillary waves were first anticipated by Smoluchowski [215] which were later given a theoretical framework known as Capillary Wave Theory (CWT) [214]. Using CWT, the solid-liquid interface has been studied for various model systems and interfaces like hard spheres [216], nickel [217], polymer mixtures [218], colloid-polymer mixtures [219], metallic mixtures [220], Ising Model [221], Asakura-Oosawa model for liquid-vapor interfaces [213], and nematic-isotropic interface [214,76,87]. CWT is based on finite-size effects and only applied

for a non-faceted interface.

The interfacial undulations cost free energy and are associated with thermal energy, interfacial tension, bending rigidity, etc. In the simplest case, the ⁷⁸ free energy cost of the interfacial area due to the undulations gives the capillary wave spectrum. According to the CWT, the mean-squared interfacial width (w) diverges logarithmically with the lateral size ($L = L_x$). Also, this width depends upon the intrinsic width, w_0 , and a cut-off parameter, l . This cut-off parameter is because CWT only accounts for the interfacial fluctuations having wavelengths larger than the typical interfacial width. According to CWT,

$$w^2 = w_0^2 + \frac{k_B T}{4\tilde{\gamma}} \ln(L) - \frac{k_B T}{4\tilde{\gamma}} \ln(l). \quad (2.23)$$

Here $\tilde{\gamma}$ is called the interfacial stiffness of the interface ³² [222]. $\tilde{\gamma}$ is related to the interfacial tension γ as $\tilde{\gamma} = \gamma + \partial^2 \gamma / \partial \theta \partial \psi$. Here the second term involving the second order partial derivatives describes the ⁶ free energy required to change the local ⁶⁵ orientation of the smectic phase, where θ and ψ are the angles between the interface normal and two orthogonal directions [223, 224]. 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 present in inhomogeneous systems change sharply within a few molecular lengths [225]. These quantities are both anisotropic and non-uniform. The pressure-tensor is one of these physical quantities which can characterize the interface mechanically. The ¹⁰ pressure-tensor is negative of the microscopic averaged stress tensor of an equilibrated fluid. The pressure of a fluid 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 are contribut-

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ing to the stress across any microscopic surface area. This uncertainty was first implicitly realized by Kirkwood, who found its two different forms with Buff [205] and Irving [226]. They acquired a formal treatment by probing the pressure over a planar surface. Later, it was explicitly described by Harasima [227], restated by Ono and Kondo [228] and its implications were explored in various works [229][230].

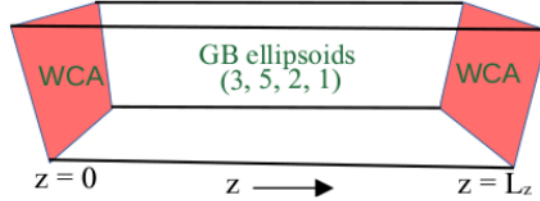


Figure 2.6: A reference image [109] of a cuboidal box containing GB (3, 5, 2, 1) ellipsoids confined by two WCA walls at the left and right z -edges of the box

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 method [201]. 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, along with the kinetic and configurational part, also include the contribution from the wall-fluid interaction. The wall interaction potential acts only in the normal direction. Therefore, it contributes only to the normal component of pressure and not to the transverse component. The kinetic contribution to P_N and the number density profile are proportional to each other [231]. 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 defined as [232]

$$P = \rho k_B T + \frac{1}{3V} \left\langle \sum_i \sum_{j>i} \mathbf{r}_{ij} \cdot \mathbf{f}_{ij} \right\rangle. \quad (2.24)$$

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

[231][233][234], the potential or virial part of the pressure tensor $P^U(z)$ can be written as

$$P^U(z) = -\frac{1}{2A} \left\langle \sum_i \sum_{j>i} \mathbf{r}_{ij} \cdot \mathbf{f}_{ij} \frac{1}{|z_{ij}|} \Theta\left(\frac{z - z_i}{z_{ij}}\right) \Theta\left(\frac{z_j - z}{z_{ij}}\right) \right\rangle. \quad (2.25)$$

For aspherical particles, the intermolecular forces include the configurational ($\mathbf{r}$) as well as the orientational ($\mathbf{u}$) contributions [235]. Now the force between two aspherical particles i and j having three orthonormal principal axes $m = 1, 2, 3$, can be calculated as [235]

$$\mathbf{f}_{ij} = -\frac{\partial U}{\partial \mathbf{r}} = -\frac{\partial U}{\partial r_{ij}} \frac{\partial r_{ij}}{\partial \mathbf{r}} - \sum_m \left\{ \frac{\partial U}{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_i)} \frac{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_i)}{\partial \mathbf{r}} + \frac{\partial U}{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_j)} \frac{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_j)}{\partial \mathbf{r}} \right\}, \quad (2.26)$$

where the intermolecular separation and the orientational unit vectors are

$$\mathbf{r} = x_{ij}\hat{\mathbf{i}} + y_{ij}\hat{\mathbf{j}} + z_{ij}\hat{\mathbf{k}}, \text{ and } r^2 = r_{ij}^2 = x_{ij}^2 + y_{ij}^2 + z_{ij}^2, \quad (2.27)$$

$$\hat{\mathbf{u}}_i = u_{ix}\hat{\mathbf{i}} + u_{iy}\hat{\mathbf{j}} + u_{iz}\hat{\mathbf{k}}, \text{ and } \hat{\mathbf{u}}_j = u_{jx}\hat{\mathbf{i}} + u_{jy}\hat{\mathbf{j}} + u_{jz}\hat{\mathbf{k}} \quad (2.28)$$

$$\begin{aligned} \frac{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_i)}{\partial \mathbf{r}} &= \frac{1}{r_{ij}} \hat{\mathbf{u}}_i = \frac{1}{r_{ij}} \{\hat{\mathbf{u}}_i - (\hat{\mathbf{u}}_i \cdot \hat{\mathbf{r}}) \hat{\mathbf{r}}\} = \frac{1}{r_{ij}} \left\{ \hat{\mathbf{u}}_i - \left(\hat{\mathbf{u}}_i \cdot \frac{\mathbf{r}}{r_{ij}} \right) \frac{\mathbf{r}}{r_{ij}} \right\} \\ &= \frac{1}{r_{ij}} \{ (u_{ix}\hat{\mathbf{i}} + u_{iy}\hat{\mathbf{j}} + u_{iz}\hat{\mathbf{k}}) - \frac{1}{r_{ij}^2} (u_{ix}x_{ij} + u_{iy}y_{ij} + u_{iz}z_{ij}) \\ &\quad (x_{ij}\hat{\mathbf{i}} + y_{ij}\hat{\mathbf{j}} + z_{ij}\hat{\mathbf{k}}) \}. \end{aligned} \quad (2.29)$$

$$\text{Hence, } \left(\frac{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_i)}{\partial \mathbf{r}} \right)_x = \frac{1}{r_{ij}} \{ u_{ix} - \frac{1}{r_{ij}^2} (u_{ix}x_{ij} + u_{iy}y_{ij} + u_{iz}z_{ij}) x_{ij} \}, \quad (2.30)$$

$$\left(\frac{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_i)}{\partial \mathbf{r}} \right)_y = \frac{1}{r_{ij}} \{ u_{iy} - \frac{1}{r_{ij}^2} (u_{ix}x_{ij} + u_{iy}y_{ij} + u_{iz}z_{ij}) y_{ij} \}, \quad (2.31)$$

$$\left(\frac{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_i)}{\partial \mathbf{r}} \right)_z = \frac{1}{r_{ij}} \{ u_{iz} - \frac{1}{r_{ij}^2} (u_{ix}x_{ij} + u_{iy}y_{ij} + u_{iz}z_{ij}) z_{ij} \}. \quad (2.32)$$

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We considered only $m = 3$ in Eq. (2.26), i.e. axis along the longest diameter of ellipsoid. According to Irving-Kirkwood [231, 233, 234] approximation, 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:

$$P_N^{IK}(z) = \rho(z)k_B T - \frac{1}{A} \left\langle \sum_i \sum_{j>i} \left[\frac{|z_{ij}|}{r_{ij}} \frac{\partial U}{\partial r} + \frac{z_{ij}}{|z_{ij}|} \left\{ \frac{\partial U}{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_i)} \left(\frac{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_i)}{\partial \mathbf{r}} \right)_z + \frac{\partial U}{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_j)} \left(\frac{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_j)}{\partial \mathbf{r}} \right)_z \right\} \right] \Theta \left(\frac{z - z_i}{z_{ij}} \right) \Theta \left(\frac{z_j - z}{z_{ij}} \right) \right\rangle, \quad (2.33)$$

$$P_T^{IK}(z) = \rho(z)k_B T - \frac{1}{2A} \left\langle \sum_i \sum_{j>i} \left[\frac{x_{ij}^2 + y_{ij}^2}{|z_{ij}| r_{ij}} \frac{\partial U}{\partial r} + \frac{1}{|z_{ij}|} \left[\frac{\partial U}{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_i)} \left\{ x_{ij} \left(\frac{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_i)}{\partial \mathbf{r}} \right)_x + y_{ij} \left(\frac{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_i)}{\partial \mathbf{r}} \right)_y \right\} + \frac{\partial U}{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_j)} \left\{ x_{ij} \left(\frac{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_j)}{\partial \mathbf{r}} \right)_x + y_{ij} \left(\frac{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_j)}{\partial \mathbf{r}} \right)_y \right\} \right] \right] \Theta \left(\frac{z - z_i}{z_{ij}} \right) \Theta \left(\frac{z_j - z}{z_{ij}} \right) \right\rangle. \quad (2.34)$$

where A is the interfacial area. Here, the first term in virial part contains derivative of potential energy (U) with 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 [92] between two particles i and j is

$$U(\hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j, \mathbf{r}) = 4\epsilon(\hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j, \hat{\mathbf{r}}) \left[\left\{ \frac{\bar{\sigma}_0}{r_{ij} - \sigma(\hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j, \hat{\mathbf{r}}) + \sigma_0} \right\}^{12} - \left\{ \frac{\sigma_0}{r_{ij} - \sigma(\hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j, \hat{\mathbf{r}}) + \sigma_0} \right\}^6 \right]. \quad (2.35)$$

To simplify the calculations, a function is defined as [39,236]

$$g(X) = \frac{6}{1-X} \left\{ \frac{(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_i + \hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_j)^2}{1+X(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j)} + \frac{(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_i - \hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_j)^2}{1-X(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j)} \right\} \quad (2.36)$$

$$= 1 - \frac{71}{2r_{ij}^2} \left\{ \frac{(\mathbf{r} \cdot \hat{\mathbf{u}}_i + \mathbf{r} \cdot \hat{\mathbf{u}}_j)^2}{1+X(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j)} + \frac{(\mathbf{r} \cdot \hat{\mathbf{u}}_i - \mathbf{r} \cdot \hat{\mathbf{u}}_j)^2}{1-X(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j)} \right\}, \quad (2.37)$$

$$\text{such that, } g(\chi) = \frac{6}{1-\chi} \left\{ \frac{(\mathbf{r} \cdot \hat{\mathbf{u}}_i + \mathbf{r} \cdot \hat{\mathbf{u}}_j)^2}{1+\chi(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j)} + \frac{(\mathbf{r} \cdot \hat{\mathbf{u}}_i - \mathbf{r} \cdot \hat{\mathbf{u}}_j)^2}{1-\chi(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j)} \right\}, \quad (2.38)$$

$$\text{and } g(\chi') = \frac{3}{1-\chi'} \left\{ \frac{(\mathbf{r} \cdot \hat{\mathbf{u}}_i + \mathbf{r} \cdot \hat{\mathbf{u}}_j)^2}{1+\chi'(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j)} + \frac{(\mathbf{r} \cdot \hat{\mathbf{u}}_i - \mathbf{r} \cdot \hat{\mathbf{u}}_j)^2}{1-\chi'(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j)} \right\}. \quad (2.39)$$

Now Eqs. (2.18) and (2.21) can be written as,

$$\sigma(\hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j, \hat{\mathbf{r}}) = \sigma_0 g(\chi)^{-1/2}, \text{ and } \epsilon_2(\hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j, \hat{\mathbf{r}}) = g(\chi'). \quad (2.40)$$

To find the derivatives of Eqs. (2.40) 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. (2.37), the derivative of $g(X)$ with respect to r (or r_{ij}) is,

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

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

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

$$\frac{\partial g(\chi)}{\partial r} = -\frac{\chi}{r_{ij}^2} \left[\frac{(\mathbf{r} \cdot \hat{\mathbf{u}}_i + \mathbf{r} \cdot \hat{\mathbf{u}}_j)}{1 + \chi(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j)} \{\cos \theta_i + \cos \theta_j\} + \frac{(\mathbf{r} \cdot \hat{\mathbf{u}}_i - \mathbf{r} \cdot \hat{\mathbf{u}}_j)}{1 - \chi(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j)} \{\cos \theta_i - \cos \theta_j\} \right] + \frac{\chi}{r_{ij}^3} \left\{ \frac{(\mathbf{r} \cdot \hat{\mathbf{u}}_i + \mathbf{r} \cdot \hat{\mathbf{u}}_j)^2}{1 + \chi(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j)} + \frac{(\mathbf{r} \cdot \hat{\mathbf{u}}_i - \mathbf{r} \cdot \hat{\mathbf{u}}_j)^2}{1 - \chi(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j)} \right\}, \quad (2.41)$$

$$\frac{\partial g(\chi')}{\partial r} = -\frac{\chi'}{r_{ij}^2} \left[\frac{(\mathbf{r} \cdot \hat{\mathbf{u}}_i + \mathbf{r} \cdot \hat{\mathbf{u}}_j)}{1 + \chi'(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j)} \{\cos \theta_i + \cos \theta_j\} + \frac{(\mathbf{r} \cdot \hat{\mathbf{u}}_i - \mathbf{r} \cdot \hat{\mathbf{u}}_j)}{1 - \chi'(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j)} \{\cos \theta_i - \cos \theta_j\} \right] + \frac{\chi'}{r_{ij}^3} \left\{ \frac{(\mathbf{r} \cdot \hat{\mathbf{u}}_i + \mathbf{r} \cdot \hat{\mathbf{u}}_j)^2}{1 + \chi'(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j)} + \frac{(\mathbf{r} \cdot \hat{\mathbf{u}}_i - \mathbf{r} \cdot \hat{\mathbf{u}}_j)^2}{1 - \chi'(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j)} \right\}. \quad (2.42)$$

Using Eq. (2.36), the derivatives of $g(\chi)$ and $g(\chi')$ with respect to $\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_i$ and $\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_j$ 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, $\frac{\partial g(\chi)}{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_i)} = -\chi \left\{ \frac{(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_i + \hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_j)}{1 + \chi(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j)} + \frac{(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_i - \hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_j)}{1 - \chi(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j)} \right\}, \quad (2.43)$

$$\frac{\partial g(\chi')}{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_i)} = -\chi' \left\{ \frac{(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_i + \hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_j)}{1 + \chi'(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j)} + \frac{(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_i - \hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_j)}{1 - \chi'(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j)} \right\}. \quad (2.44)$$

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

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

Hence, $\frac{\partial g(\chi)}{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_j)} = -\chi \left\{ \frac{(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_i + \hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_j)}{1 + \chi(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j)} - \frac{(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_i - \hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_j)}{1 - \chi(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j)} \right\}, \quad (2.45)$

$$\frac{\partial g(\chi')}{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_j)} = -\chi' \left\{ \frac{(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_i + \hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_j)}{1 + \chi'(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j)} - \frac{(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_i - \hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_j)}{1 - \chi'(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j)} \right\}. \quad (2.46)$$

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

$$\begin{aligned} \frac{\partial U}{\partial r} &= 4\epsilon_0 \epsilon_1^\nu(\hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j) \left[\mu g^{\mu-1}(\chi') \frac{\partial g(\chi')}{\partial r} \left\{ \left(\frac{1}{R} \right)^{12} - \left(\frac{1}{R} \right)^6 \right\} + \right. \\ &\quad \left. g^\mu(\chi') (6R^{-7} - 12R^{-13}) \frac{\partial R}{\partial r} \right], \end{aligned} \quad (2.47)$$

$$\begin{aligned} \frac{\partial U}{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_i)} &= 4\epsilon_0 \epsilon_1^\nu(\hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j) \left[\mu g^{\mu-1}(\chi') \frac{\partial g(\chi')}{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_i)} \left\{ \left(\frac{1}{R} \right)^{12} - \left(\frac{1}{R} \right)^6 \right\} + \right. \\ &\quad \left. g^\mu(\chi') (6R^{-7} - 12R^{-13}) \frac{\partial R}{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_i)} \right], \end{aligned} \quad (2.48)$$

$$\begin{aligned} \frac{\partial U}{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_j)} &= 4\epsilon_0 \epsilon_1^\nu(\hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j) \left[\mu g^{\mu-1}(\chi') \frac{\partial g(\chi')}{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_j)} \left\{ \left(\frac{1}{R} \right)^{12} - \left(\frac{1}{R} \right)^6 \right\} + \right. \\ &\quad \left. g^\mu(\chi') (6R^{-7} - 12R^{-13}) \frac{\partial R}{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_j)} \right]. \end{aligned} \quad (2.49)$$

The derivatives of R (Eq. (2.17)) with respect to r , $\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_i$ and $\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_j$ are,

$$\frac{\partial R}{\partial r} = \frac{1}{\sigma_0} \left\{ 1 + \frac{\sigma_0}{2} g^{-3/2}(\chi) \frac{\partial g(\chi)}{\partial r} \right\}, \quad (2.50)$$

SECTION 2.6: COMPUTATION OF THE INTERFACIAL PROPERTIES

$$\begin{aligned}
 \frac{\partial R}{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_i)} &= \frac{1}{\sigma_0} \left\{ \frac{\partial r}{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_i)} - \frac{-\sigma_0}{2} g(\chi)^{-3/2} \frac{\partial g(\chi)}{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_i)} + \frac{\partial \sigma_0}{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_i)} \right\} \\
 &= \frac{1}{\sigma_0} \left\{ 0 + \frac{\sigma_0}{2} g(\chi)^{-3/2} \frac{\partial g(\chi)}{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_i)} + 0 \right\} \\
 &= \frac{1}{\sigma_0} \left\{ \frac{\sigma_0}{2} g(\chi)^{-3/2} \frac{\partial g(\chi)}{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_i)} \right\} = \frac{1}{2} g(\chi)^{-3/2} \frac{\partial g(\chi)}{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_i)}. \quad (2.51)
 \end{aligned}$$

$$\text{Similarly, } \frac{\partial R}{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_j)} = \frac{1}{2} g(\chi)^{-3/2} \frac{\partial g(\chi)}{\partial(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_j)}. \quad (2.52)$$

Hence, using above equations, P_N^{IK} (Eq. (2.33)) and P_T^{IK} (Eq. (2.34)) can be calculated. Now, the pressures 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,

$$P_{LW}(z) = -\epsilon_W \sum_i \frac{\partial V_{WCA}}{\partial z_i} \Theta(z_i - z) \Theta(z - z_{LW}), \quad (2.53)$$

$$P_{RW}(z) = -\epsilon_W \sum_i \frac{\partial V_{WCA}}{\partial z_i} \Theta(z_{RW} - z) \Theta(z - z_i). \quad (2.54)$$

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

$$P_N(z) = P_N^{IK}(z) + (P_{LW}(z) + P_{RW}(z))/A, \quad (2.55)$$

$$P_T(z) = P_T^{IK}(z). \quad (2.56)$$

In reduced units, the normal pressure tensor component is $P_N v_m / (k_B T)$, and the tangential pressure tensor component is $P_T v_m / (k_B T)$ [237], where $v_m = \pi \sigma_0^3 / 2$ is the volume of ellipsoidal molecule ($\sigma_{ee} = 3\sigma_0$, and $\sigma_{ss} = 1\sigma_0$). Using pressure-tensor relation, the wall-fluid interfacial tension γ is calculated as [231, 233, 234, 201]

$$\gamma = \frac{1}{2} \int_{z_{LW}}^{z_{RW}} (P_N(z) - P_T(z)) dz. \quad (2.57)$$

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 (central region) packing fraction [237]. In Eq. (2.57), the factor 2 in the denominator is to account for two interfaces near the left and right walls. In our case, $z_{LW} = 0$ and $z_{RW} = L_z$ (Fig. 2.6). Using PT method, the surface tension for various unconfined model systems such as liquid-vapor interface in LJ fluid [238][225], isotropic-nematic interface in hard and soft ellipsoids [95], vapor-isotropic [239] and vapor-nematic interface in GB fluid [240][239] has been calculated. It has also been successfully used for confined model systems such as polymeric thin films confined by two repulsive walls [231], hard spheres enclosed by WCA walls [201], and hard spherocylinders near hard walls [237]. Due to the successful implementation of the PT method in various model systems, we have also used this method¹⁰ to determine the interfacial properties of the confined GB system.

Chapter 3

Interfacial stiffness of Gay-Berne nematic-smectic B interface

3.1 Introduction

During the nucleation and growth phenomenon, ¹²⁴a well-defined interface ³³separates a nucleating phase from the surrounding mother phase, and the knowledge of the properties of such interfaces is crucial for better material processing. The interfacial phenomenon has been extensively studied in the systems of hard-spheres, one-component Asakura-Oosawa model(AO) [219], Ising model [241], colloid-polymer mixture [202,242] and Lennard Jones fluid [243]. The interfacial ¹¹⁰properties, such as the interfacial tension or stiffness, of the interfaces formed can be calculated using various methods such as thermodynamic integration method [244], capillary wave theory [219], expanded ensemble simulation method [245], etc. In the case of a LC material, it is expected that the shape anisotropy of liquid crystalline particles would result in more intricate interfacial properties. Now, the literature is full of exhaustive studies addressing the isotropic-nematic interfacial properties [86,94,97,87]. However, much remains unknown about the nematic-smectic (nm-sm) interface. In this chapter, we have addressed and calculated the interfacial stiffness of a nematic-smecticB (nm-smB) interface. A nematic-smectic (nm-sm) interface can be observed by simulating an nm-sm phase coexistence, and that is possible when the nm-sm

phase transition is of the first order. However, the nature of the phase transitions between the nematic and smectic (A, B, or C) phases is not clear yet; some literature argues for a continuous phase transition [246, 247, 248] while others contest the same [249]. From computer simulations [174, 193, 190, 250, 251], theoretical [194, 252, 253, 254, 255] and experimental works [256, 257] only this much is clear so far that, the type of phase transition between nematic and smectic phases depend on several factors, namely, the elongation or aspect ratio of the constituents, 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, and thus making the nm-smB coexistence region a possibility [174]. Here we have simulated LC mesogens with a low aspect ratio of $\kappa = 3$, and indeed, we were able to observe the nm-smB phase coexistence. Here, the interfacial properties depend upon several factors like the orientational symmetry between the two coexisting phases, the anchoring of particles near the interface, the extent of shape anisotropy, temperature, and particle interactions [97, 51, 76, 174, 109]. 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 the interface with parallel anchoring [76], and there is zero fluctuation (i.e., a smooth interface) in the case of an LC interface consisting of particles with infinite elongation [89]. Moreover, between the isotropic-nm and nm-sm interface, the latter is expected to be comparatively smoother with less fluctuation owing to the two phases' higher orientational symmetry. Our simulations show that the nm-smB interface is rough, fluctuating, and its position is not sharply defined. The later observations made it possible for us to use the Capillary Wave Theory (CWT) analysis of the interfacial fluctuations to determine the interfacial stiffness of the nm-smB interface, as has already been done in earlier studies for different systems [216, 219].

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

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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 with each other, the simulations are done following a recipe consisting of the 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 ¹³ velocities and orientations of the 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 ⁵⁸ 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 (NVT ensemble) ¹ 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 also to lower the overall density of the system. This new system, now having $N = \lambda N'$ number of particles, is ⁵⁵ then simulated again under the modified NVT -ensemble for 5×10^6 MD steps. At the end of the third step, the phase of the system 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 a nematic phase (represented by blue colour) and the other half is in a smectic-B phase (represented by pink colour) for all the system sizes taken. During a simulation, ³² periodic boundary conditions are applied along all three directions and the MD time-step size we have 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 been able to obtain well-equilibrated systems with nematic phase coexisting with the smectic-B phase. As periodic boundary conditions are applied during the simulations, two phases are separated by two interfaces along the z -directions. The snapshots on the left panels in Fig. 3.1 are showing 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 not only has long-range orientational order but also positional order owing to the layered arrangement of its constituent particles. The corresponding snapshots on the right side of Fig. 3.1 are only showing the smectic-B part. We use the local bond order parameter, $Q_l(i)$ as introduced by Steinhardt *et al.* [258] 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 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 [259]

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

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

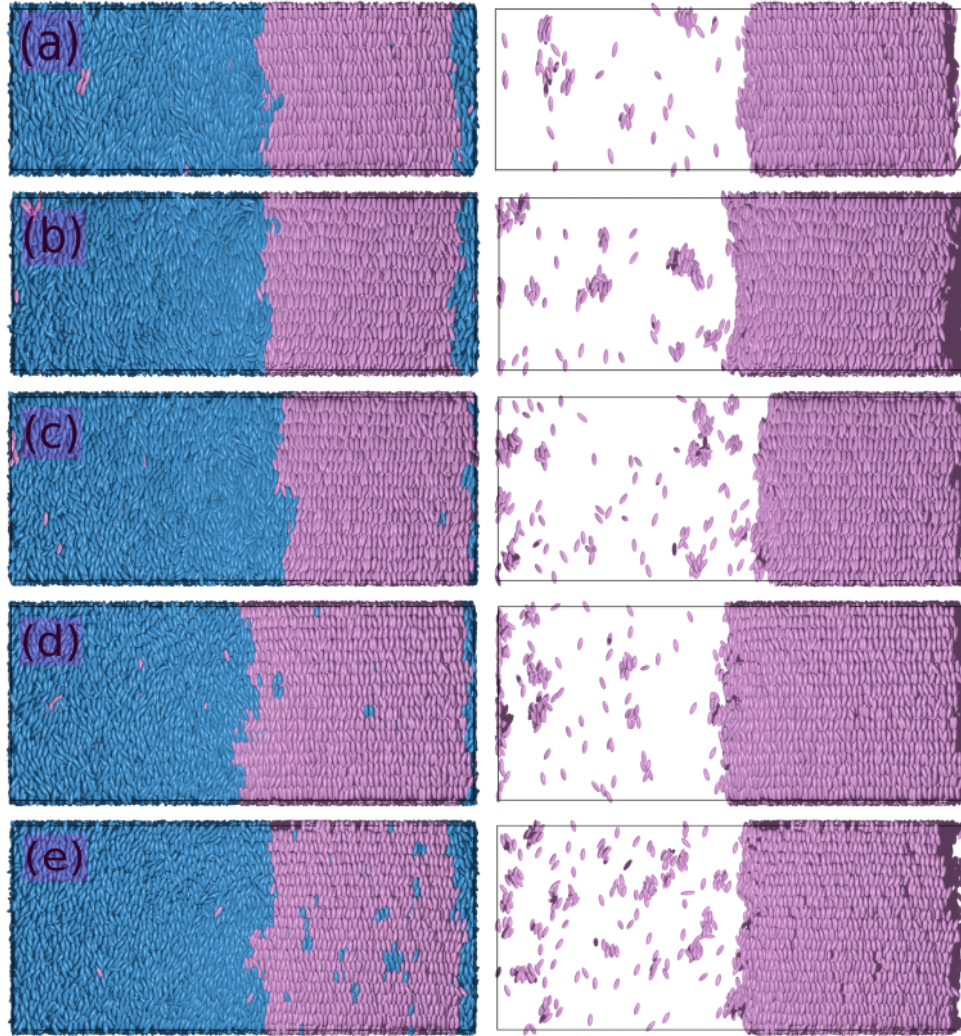


Figure 3.1: Left side snapshots: showing the coexistence of nematic (blue) and smectic-B (pink) phases; Right side snapshots: showing only the smectic-B phase. The particle identification is done by using local bond order parameters $q_6 q_6[i]$. The temperature and coexistence density are $T = 1.0$ 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 $L_z \simeq 97$

We take $l = 6$ and find $q_6 q_6(i)$ ²⁷ for all the 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 $Z_i \geq 12$ ²¹⁹. The nearest neighbors count (Z_i) for each particle is calculated by 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 the particles in the two phases but also on the relative angle between the directors of the two phases^{109,107,108,222,76}. The data presented here are for all the cases when two⁴ 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 phase directors) will be comparably more stable than the other anchorings. In fact, in significant fractions of our simulations, we have indeed observed the planar anchoring. But, the precise determination of minimum energy anchoring still remains to be explored. Therefore, we have consciously chosen to analyze only the cases similar to the systems as shown in Fig. 3.1 by running the simulations with different initial configurations. In the Fig. 3.2 we have plotted the angular difference between the 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 that we have analyzed for this report. It is clear that two⁴ directors are nearly parallel to each other as the polar angular difference between them are close to zero. To check the stability of the coexistence, we have measured the width of the nematic phase (Δw_{nm}) and are plotted versus the time as⁵⁰ shown in Fig. 3.3. The width of the nematic phase on average remains constant for 2×10^6 MD time steps. However, the amplitude of fluctuations in the domain width or the phase breathing width decreases¹⁷ 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.*^{260,261,262}. 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

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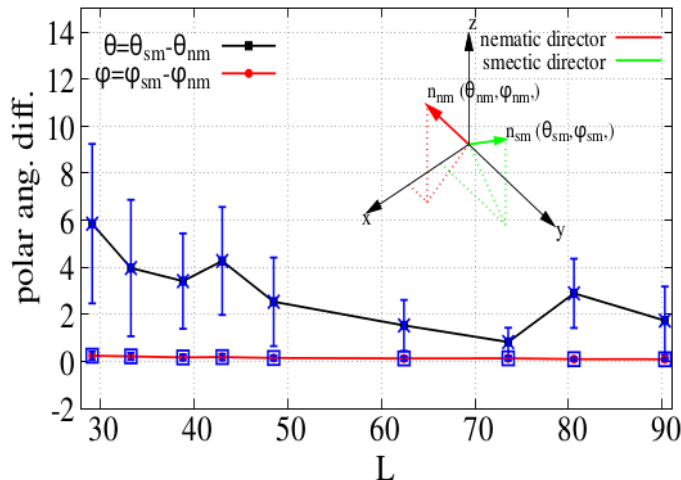


Figure 3.2: The relative angle between the nematic and smectic directors of the system with the nm-smB interface for various system sizes. θ (circles) and ϕ (squares) represent the difference in the polar angles θ and ϕ respectively of nematic ($\mathbf{n}_{nm}$) and smectic ($\mathbf{n}_{sm}$) directors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

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 shows the similar dependence in our case too. The small-amplitude nearly periodic oscillations of the nematic width indicate the presence of a beautiful breathing phenomenon of the coexisting phases in the system. Such a breathing phenomenon is a result of thermally excited fluctuations occurring in the interface separating the two phases, resulting in the formation of capillary waves across the same. We have also evaluated the time autocorrelation of the nematic domain width fluctuations as shown in Fig. 3.4. With time, the correlation for nematic width reaches zero at $\tau = 50$, which means that there is no correlation after $\tau = 50$. Therefore, the time correlation of domain width fluctuations is short-range (exponentially decaying). Moreover, these domain fluctuations are also system size-dependent which is characterized in the inset of the Fig. 3.3

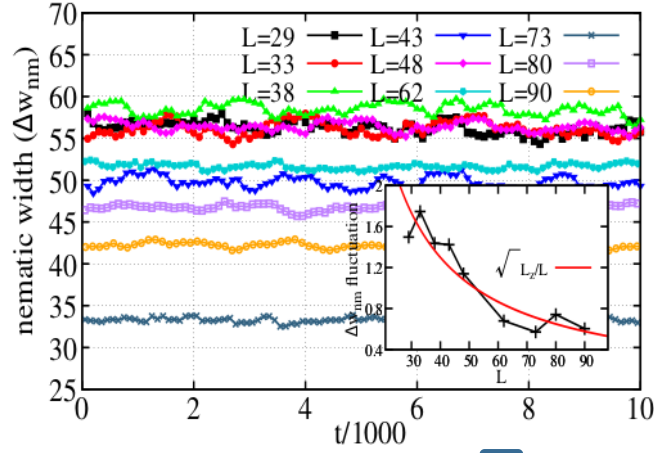


Figure 3.3: The variation of the width of the part of the system that is in the nematic phase with time. This clearly shows the breathing phenomenon wherein the width of two coexisting phases are oscillating, but remaining stable with a fixed size on average. The data is at overall density $\rho_{co}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

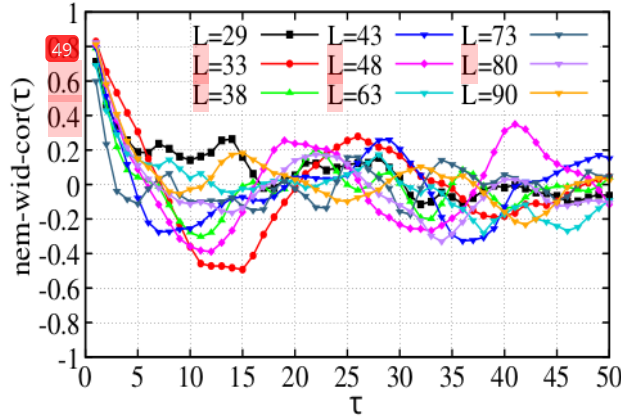


Figure 3.4: The correlation of nematic width with time for all system sizes

3.2.2 Coexistence density range

The coexistence density (ρ_{co}) range for the nematic and smectic-B phases is bounded between the freezing density (ρ_{nm}^f) of the nematic phase into a smectic-B phase and the melting density (ρ_{sm}^m) of a smectic-B phase into a nematic phase, i.e. $\rho_{nm}^f < \rho_{co} < \rho_{sm}^m$. To determine the range of ρ_{co} , we used the density profile of a system with two

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coexisting phases [216, 76, 240]. To this end, we have calculated the density profiles for all the system sizes taken and are shown in Fig. 3.5. To compute the density

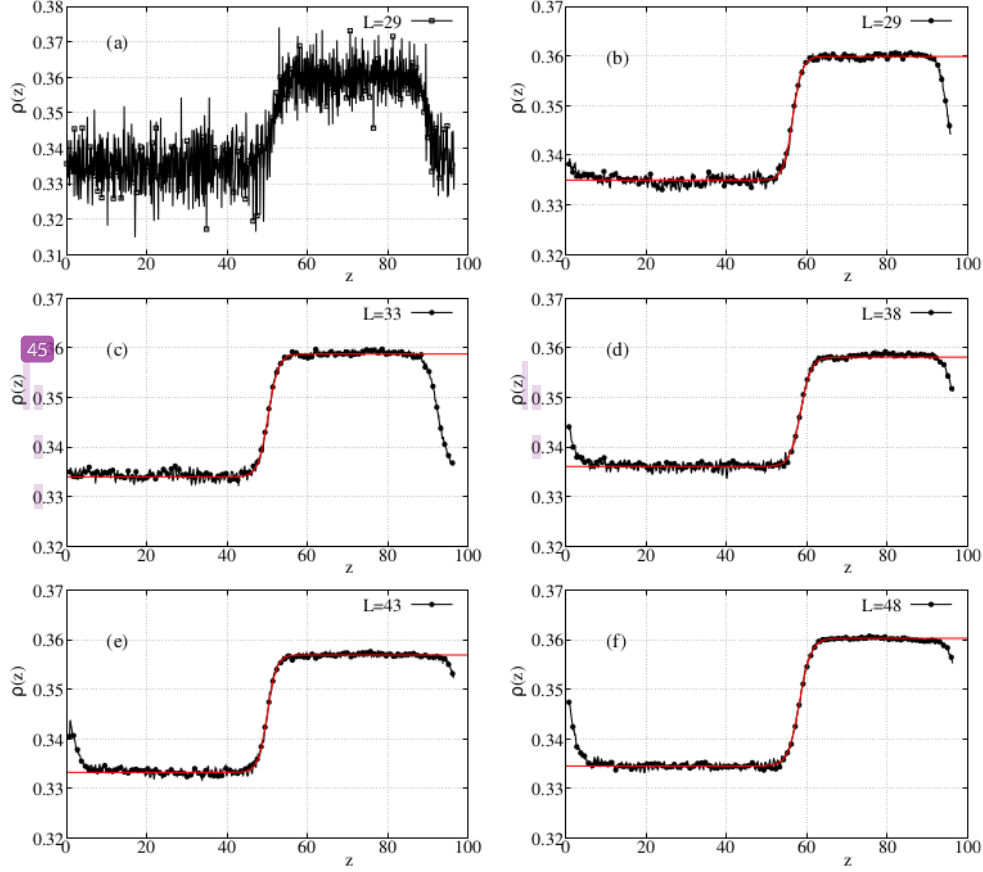


Figure 3.5: (a) Average density profile of the system of size $L = 29$ at temperature $T = 1.0$ and overall density, $\rho_{co} = 0.345$. (b)-(f) Running averaged density profiles (black solid curve with filled circle) and hyperbolic tangent fit (red solid line) corresponding to various systems with sizes $L = 29, 33, 38, 43, 48$ and all having $L_z \simeq 97$ at temperature $T = 1.0$ and overall system density, $\rho_{co} = 0.345$

profile transverse to the interface, the system is sliced into 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 time-step 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 the 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-sequences, i.e. only 100 configurations, as shown in Fig. 3.5(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. 3.5(b-f) for the first sub-sequence of 100 configurations. The process is repeated separately for all the sub-sequences and the respective 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 respective fitting parameters obtained from the fits of all the sub-sequences. As there are two interfaces present in the system due to the periodic boundary conditions, the same steps are followed for both the interfaces and the averaging is done accordingly. The coexistence densities of the nematic ($\rho_{nm}^f = A - B$) and smectic-B ($\rho_{sm}^m = A + B$) phases are listed in the Table 3.1. The systems with the 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 both the phases would be coexisting within the system. Similarly, if the system's overall density is gradually increased from ρ_{nm}^f to ρ_{sm}^m then the width of the nematic phase would gradually decrease and that of the smectic-B phase would increase by following the simple lever rule of a binary mixture. The same has been verified by running several independent simulations at different coexistence densities

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$\rho_{nm}^f < \rho_{co} < \rho_{sm}^m$. We have also confirmed the coexistence range as obtained by the density profile analysis by running independent simulations with systems at overall density outside of the coexistence range. It is to be noted here that the

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: Range of coexistence densities for nm and smB phases at $T = 1.0$ and $\rho_{co} = 0.345$ for different system sizes using density profiles

coexistence range at $T = 1.0$ as reported here is slightly different from that reported by Miguel [35]. Though Miguel did not report the range exactly for $T = 1.0$, but did for $T = 0.95$ as $\rho_{nm}^f = 0.3449$ 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. However, because we have taken two orders of magnitude larger system which improves the statistical averages, we believe that the nm-smB coexistence range, as reported in Table 3.1 would be an improvement over the earlier reported values.

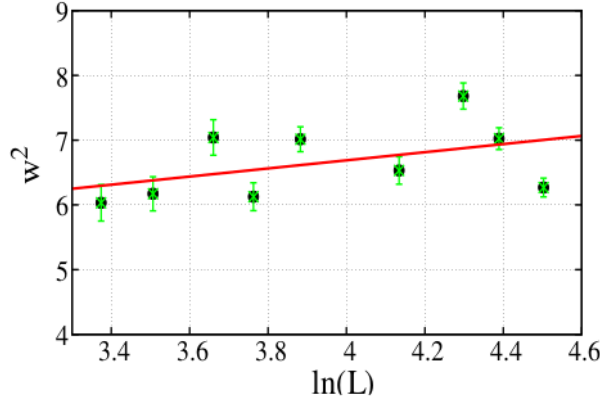


Figure 3.6: Mean squared interfacial width versus natural logarithm of lateral size of box with $L = 29, 33, 38, 43, 48, 62, 73, 80, 90$ with standard deviation in the interfacial width

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, the 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 $w_0^2 - (k_B T/4\tilde{\gamma}) \ln(l)$. As shown in Fig. 3.6 the mean-squared interfacial widths (w^2) as calculated from the density profiles are plotted versus the corresponding $\ln(L)$. The data is then fitted to a straight line (solid red line) and calculated its slope (m) which is then used to calculate the interfacial stiffness as $\tilde{\gamma} = k_B T/4m$. In reduced units, $\tilde{\gamma}$ comes out to be $0.39861k_B T/\sigma_{ee}^2 = 0.04429/\sigma_{ss}^2$ (where σ_{ee} and σ_{ss} are the length and diameter of GB ellipsoid).

3.3 Summary and conclusion

This chapter presents a molecular dynamics simulation study of the nm-smB phase coexistence of thermotropic Gay-Berne liquid crystals. We found that computationally it is very inefficient to obtain a well-equilibrated nm-smB phase coexistence in a finite volume. Hence, we have developed a simple three-step-recipe to obtain a coexistence in a fairly efficient manner. By analyzing the coexisting phases' density profiles along a direction transverse to the interface, the coexistence range of the nematic and smectic-B phases at $T = 1.0$ is calculated. Then, using the local bond order parameter $q_6 q_6$, 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 the CWT analysis of the interface, the interfacial stiffness of the nm-smB interface is obtained which comes out to be $\tilde{\gamma}_{nm-smB} = 0.39861k_B T/\sigma_{ee}^2 = 0.04429/\sigma_{ss}^2$. It is important to note that such studies are an important endeavour because ac-

SECTION 3.3: SUMMARY AND CONCLUSION

curate estimation of interfacial stiffness is indispensable for applications in crystal nucleation and growth phenomena.

Chapter 4

Interfacial tension between Gay-Berne isotropic fluid and wall

4.1 Introduction

Due to their several technological applications, the confined LCs have been extensively studied [263] using experiments [71, 264, 124], computer simulations [265, 266, 144] and various theoretical models [124, 267, 143]. In confined LCs, when an isotropic phase approaches a nematic or smectic phase, an ordered surface layer is developed with a finite or infinite limiting thickness, known as the orientational wetting phenomenon [268]. 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 [71, 265]. This mechanism of modification of bulk alignment according to the surface alignment is known as 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 [265]. In literature, there are numerous studies available for LC model systems confined by different surface potentials [265]. For example, the study of soft ellipsoids near hard rough walls [269, 270], hard ellipsoids [271, 272, 273, 274] and rods [275, 276] near hard walls, hard colloidal rods near a soft wall [277], simple LC model near smooth wall [278], hard Gaussian overlap

particles confined by slab geometry [263, 279], hard spherocylinders near parallel walls [280], hard planar walls [281, 237] and hard spherical cavity [282], and so on.

Depending upon the nature of the surface, LCs may favor or restrain different molecular ordering [283]. For instance, free surfaces in free-standing films encourage smectic (A or C) phase. In contrast, the surface in small pores promotes nematic phase [283]. Further depending upon the interaction potential between surface and LC molecules [265], homeotropic (perpendicular to the surface) [284, 143, 119, 285], planar (parallel to the surface) [281, 265] and tilted [286, 263] alignments have been observed. For instance, Allen *et al.* [273] observed the homeotropic surface anchoring of hard ellipsoids with a smooth and hard repulsive wall. In contrast, the planar ordering was observed for hard spherocylinders near smooth, hard wall [281]. The widely used LC model is the Gay-Berne (GB) potential model. The GB molecules enclosed in slab geometry [180, 287, 288, 289, 269, 290, 291, 292], structured walls [293], spherical cavity [294], and cylindrical nanopores [295] have been well studied. The confinement of GB ellipsoids by the parallel surfaces have resulted into tilted [296, 287], homeotropic [297] and planar anchoring states [298, 299, 288]. In this Chapter, we are presenting the study of determining the interfacial tension (γ_{WI}^*) of an interface between GB isotropic phase and WCA wall. Among various parameters, a set of GB parameters (3, 5, 2, 1) has been widely used in the slab confined GB molecules [180, 287, 300, 301]. 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 [34].

4.1.1 Simulation details

The data presented here are collected from the canonical ensemble simulations with MD time-step size, $\Delta t = 0.005$ units at temperature, $T = 1$ units. To carry out the simulations, a cuboidal box ($L_x \times L_y \times L_z$) filled with GB ellipsoids is taken such that the lengths of 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

SECTION 4.1: INTRODUCTION

maintain a large separation between walls so that walls do not interact with each other through the bulk fluid. Therefore when L_z is large enough, we expect that the bulk isotropic fluid would be similar to the corresponding fluid in the absence of confining walls [201]. The simulations are performed using a three-step recipe. In the first step, we take an isotropic box that has ¹²³ 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 chosen randomly. 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 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 is deleted (mostly near the walls) from the simulation box to prepare systems with lower densities. The third step is repeated to achieve confined isotropic bulk phases at different number densities. Following this, the data is collected after every 100 MD time-steps during a run of 10^6 MD time-steps, resulting in 10^3 well-equilibrated confined configurations. ¹¹⁸ In order to study the finite-size effects, the above three-step recipe is also used for a larger system size ($L \approx L_z/3$). The effect of varying WCA potential's strength (ϵ_W) on the interface between WCA wall and GB ellipsoids is also analyzed by using four different $\epsilon_W = 1, 4, 7$, and $10 \epsilon_0$ with $\sigma_W = 1.0 \sigma_0$.

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 overall number densities (ρ) at temperature $T = 1$ units for two system sizes with $L \approx L_z/2$ and $L \approx L_z/3$. Due to 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), it is observed that the effect of wall is more prominent at higher densities than lower ones. For instance, the snapshot (Fig. 4.1(a)) of very low overall number density $\rho = 0.1000$ (bulk or central density, $\rho_b = 0.1034$) indicates the dewetting of wall by GB ellipsoids with the whole isotropic phase (having no positional and orientational order). This implies that at very low densities, wall does not have any significant effect on its nearby fluid. But as density increases, the wall's influence gets stronger and particles starts orienting normal to the wall surface (Fig. 4.3). The enhancing impact of wall with ρ is evident from the snapshots of 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) appears in which the GB particles align homeotropically near the wall (i.e. particles' director is normal to the wall). As the bulk density approaches the isotropic-nematic phase transition density, the bulk particles does not remain disordered anymore but starts aligning in a particular direction. The density $\rho = 0.3090$ ($\rho_b = 0.3047$) is very close to the isotropic-nematic phase transition as observed from the orientational order profile (Section 4.2.2). At the isotropic-nematic transition [35] density $\rho = 0.3135$ ($\rho_b = 0.3088$) (Fig. 4.1(f)), the particles near the smectic layers and in bulk, start attaining an orientational order. In the present report, we mainly focus on the interface between WCA wall and the bulk isotropic phase, i.e. upto $\rho = 0.3090$ ($\rho_b = 0.3047$).

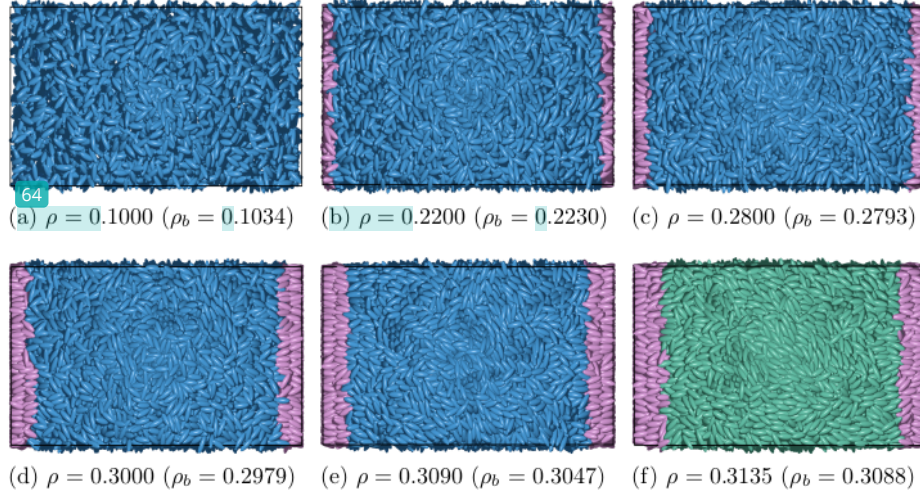


Figure 4.1: The snapshots (yz -view) of system size, $L = 27.9841$ and $L_z = 58.2131$, are shown with wall at various number densities using povray: bulk isotropic (shown by blue color) phase with (a) no wall-induced order, (b) some order induced by wall, (c), (d), (e) smectic (shown by light pink color) 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 identify the smectic-like ordered layers near the wall from the bulk phase, we have colored the particles differently which are within the distance of strong oscillations (layering) in the density profile (done for visual clarity)

The similar effect of wall upon increasing ρ can be seen in the profiles of ² 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 ⁹ pressure-tensor profiles, the system is divided into bins of size equal to 0.03 units along z -direction, and then the P_N and P_T (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 ¹⁰ component, P_N , is constant irrespective of the distance from the wall, which is essential to maintain mechanical stability [231, 237]. The normal pressure, P_N , coincides with the bulk tangential pressure $P_T(z)$ and corresponds to the bulk scalar pressure. However, the tangential component $P_T(z)$ depends upon the position z from the wall. The sharp peaks in $P_T(z)$ in the vicinity of a wall (Fig. 4.2) indicate the wetting of the wall by an ordered (orientational and/or positional)

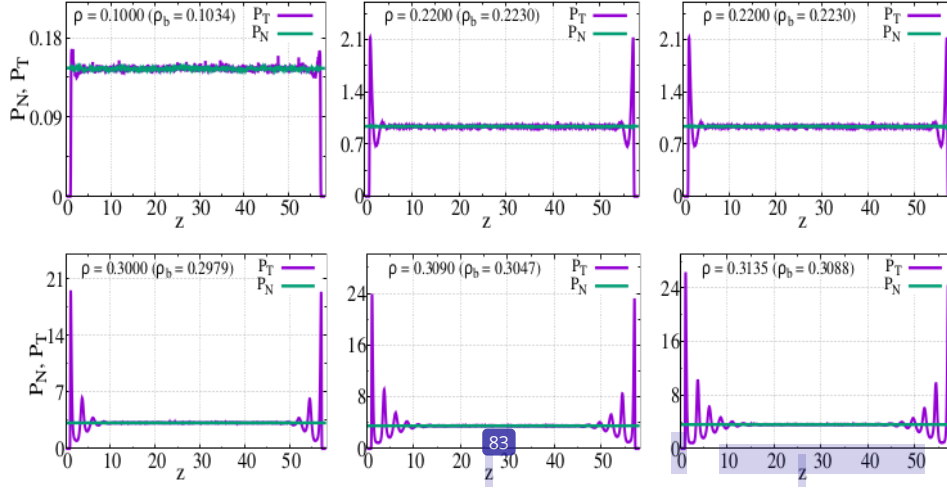


Figure 4.2: The reduced pressure tensor components (P_N and P_T) along z for $L = 27.9841$ and $L_z = 58.2131$ system size for various number densities

phase. These oscillations in $P_T(z)$ get stronger as the order near the wall increases upon increasing ρ .

To numerically elucidate the wetting of wall, the nematic (orientational) order parameter, S_W , is calculated within the distance of $6\sigma_0$ (nearly two smectic layers) from both the walls for 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 .

As is apparent from the orientational order plot (Fig. 4.3), the orientational order in the vicinity of wall increases with increasing 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 ρ_b increases, the particles' orientational order near the wall increases (as appears from the snapshot of $\rho_b = 0.2603$ in Fig. 4.3), 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 $\rho_b = 0.2796$ (Fig. 4.1(c)) where $S_W \approx 0.41$ (Table 4.1). Such a low value of S_W is because in our calculation, 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

SECTION 4.2: RESULTS AND DISCUSSION

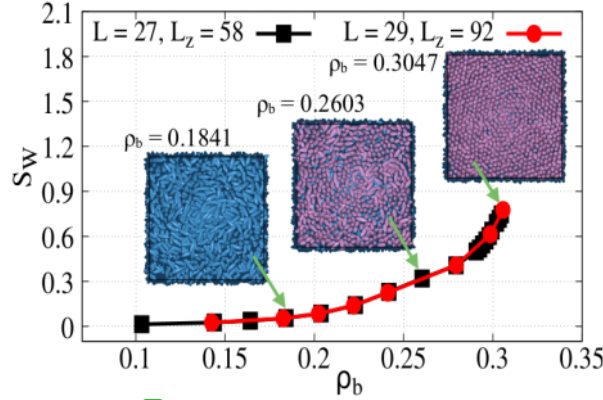


Figure 4.3: The variation in the nematic order parameter calculated within the distance of $6\sigma_0$ (nearly two smectic layers) from both the walls upon increasing bulk number density ρ_b for two system sizes. The snapshots shown here are the xy -view of GB particles near the wall

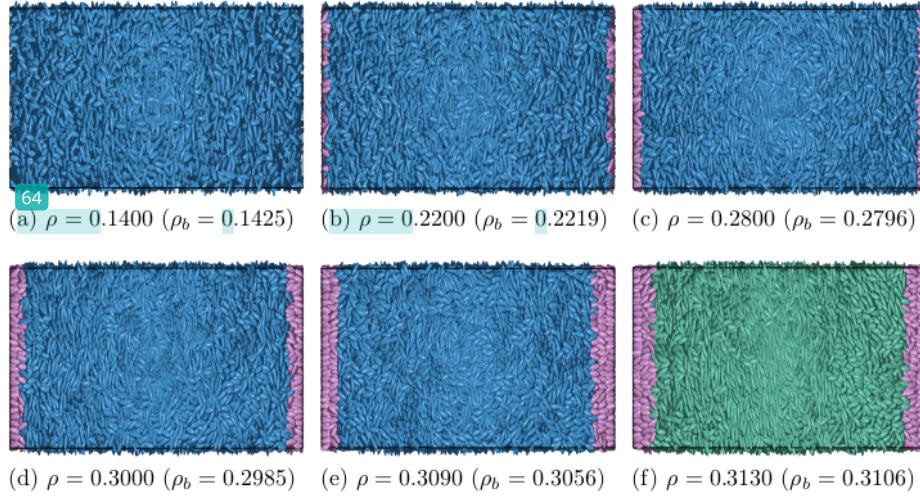


Figure 4.4: The snapshots (yz -view) of system size, $L = 29.4111$ and $L_z = 91.8788$, are shown with wall at various number densities using povray: bulk isotropic (shown by blue color) phase with (a) no wall-induced order, (b) some order induced by wall, (c), (d), (e) smectic (shown by light pink color)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

layers increases. As is observed at $\rho_b = 0.3047$ (Fig. 4.1(e)), there are more than one smectic layers near the wall due to which S_W increases to around 0.75 (Table 4.1). The orientational order in bulk (S_b) is also calculated as shown in Table 4.1

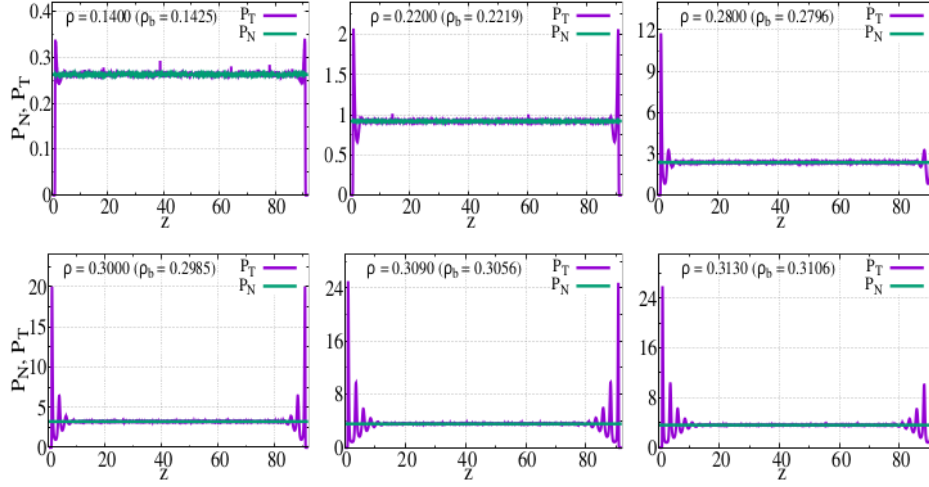


Figure 4.5: The reduced pressure tensor components (P_N and P_T) along z for $L = 29.4111$ and $L_z = 91.8788$ system sizes for various number densities

The very low values of S_b indicate ¹¹⁴ that the bulk system is in the isotropic phase till $\rho_b = 0.3047$. At bulk isotropic-nematic transition density $\rho_b = 0.3088$, S_b comes out to be 0.315, which indicates the presence of some orientational order in bulk.

³⁶ In order to understand the effect of system size on the confined GB ellipsoids, the similar simulations and calculations are performed for larger system size, i.e., $L = 29.4111$, and $L_z = 91.8788$ ($L \approx L_z/3$). The snapshots, the corresponding pressure tensor profiles, and the nematic order plot for large system size are shown in Figs. ^{4.4} ^{4.5} and ^{4.3} respectively. From snapshots, profiles, and plots, it is clear that this system behaves similar 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 of the confined GB isotropic fluid system.

4.2.2 Density and local orientational order profiles

²⁶ Anchoring plays a key role in determining the interfacial properties. Different type of anchoring (homeotropic/ planar/ tilted) results in different values of the interfacial tension (γ) or stiffness ⁹⁷. Therefore before estimating γ , ² it is crucial to understand the type of anchoring of GB particles with the wall. From Figs. ^{4.1} and ^{4.4} it can

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be seen that the bulk particles are oriented randomly, but the particles near the wall are oriented normal to the wall, i.e., homeotropic anchoring. In other words, the wall-normal ⁵ is parallel to the director of the wall-induced ordered (smectic) phase. Numerically, the wall-effectuated structural changes are observed using the number

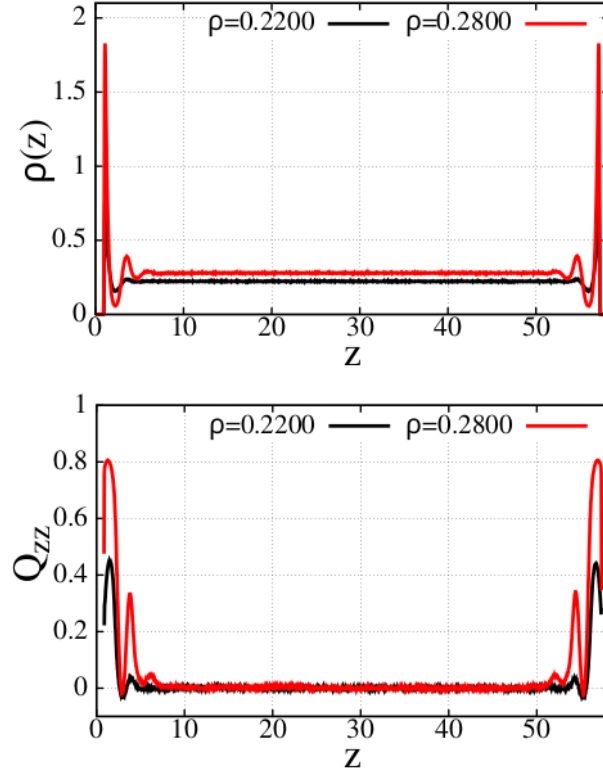


Figure 4.6: For $L = 27.9841$ and $L_z = 58.2131$ system sizes, the number density (top graph) and local orientational order profiles (bottom graph) for two overall densities are exhibiting the homeotropic alignment of particles near the wall

⁶⁹ density $\rho(z)$, and orientational order $Q_{zz}(z)$ profiles. The orientational order profile along z (or normal to the walls) ²⁶⁵ is calculated as

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

⁶⁷ where $N(z)$ is the number of particles in the layer and $\mathbf{u}_i$ is the orientational vector of i^{th} particle. The profiles $\rho(z)$ and $Q_{zz}(z)$ for smaller system size ($L = 27.9841$,

$L_z = 58.2131$) 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 showing the intrinsic coupling between number density and orientational order parameter. It confirms the homeotropic alignment 265 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. Here, the local orientational order profiles $Q_{zz}(z)$ plotted at different ρ for both the system sizes (Fig. 4.7) are providing an information about the onset of the orientational order in an 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 isotropic phase starts orienting in a particular

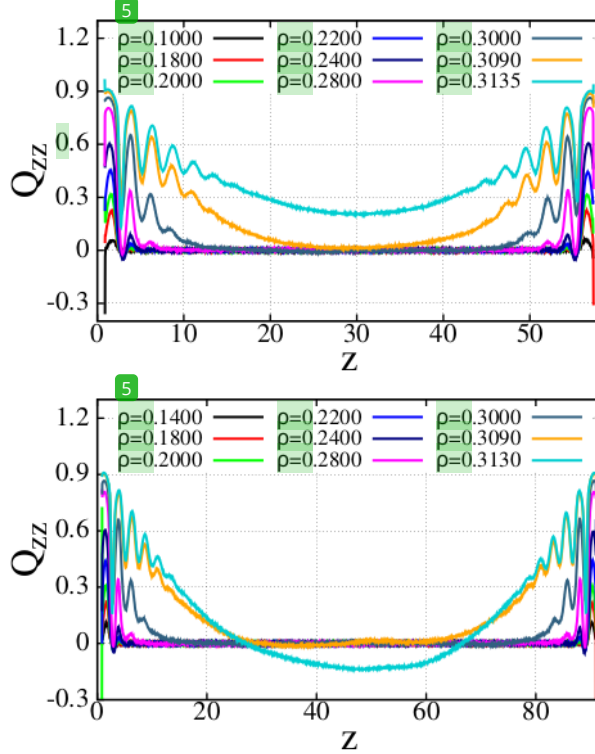


Figure 4.7: The local orientational order profiles $Q_{zz}(z)$ for system size, (a) $L = 27.9841$ and $L_z = 58.2131$, (b) $L = 29.4111$ and $L_z = 91.8788$, for various number densities with bulk isotropic phase

direction, $Q_{zz}(z)$ starts deviating from zero 291,302,303. Now, depending upon the particles' orientations, i.e., they are along the wall-normal (or z -direction) or

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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 normal to the wall [265]. However, at the isotropic-nematic phase transition density, $Q_{zz}(z)$ is positive for smaller system size and negative for larger system size. Therefore for the bulk isotropic phase, no system-size effect is observed for the system sizes taken. However, the system sizes we considered have considerable effects on the GB LC system at the isotropic-nematic transition densities 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 pressure-tensor formula (Eq. (2.57)) for $\epsilon_W = \epsilon_0$ for two system sizes. 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 [237]. At very low density ($\rho_b = 0.1034$), γ_{WI}^* is very small due to dewetting of wall by bulk isotropic phase. As density increases, the confinement due to the smooth repulsive wall influences its nearby particles to start orienting along the wall normal without much effect on the bulk disorderd phase, and hence interfacial tension increases. 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 results in further reduction of γ_{WI}^* upon increasing ρ [237]. 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 [71]. As a result, the presence of a strong smectic layer reduces the energy required to further wet the wall, and thus stimulates the wetting process. Both the system sizes are exhibiting the similar interfacial tensions with the bulk isotropic phase.

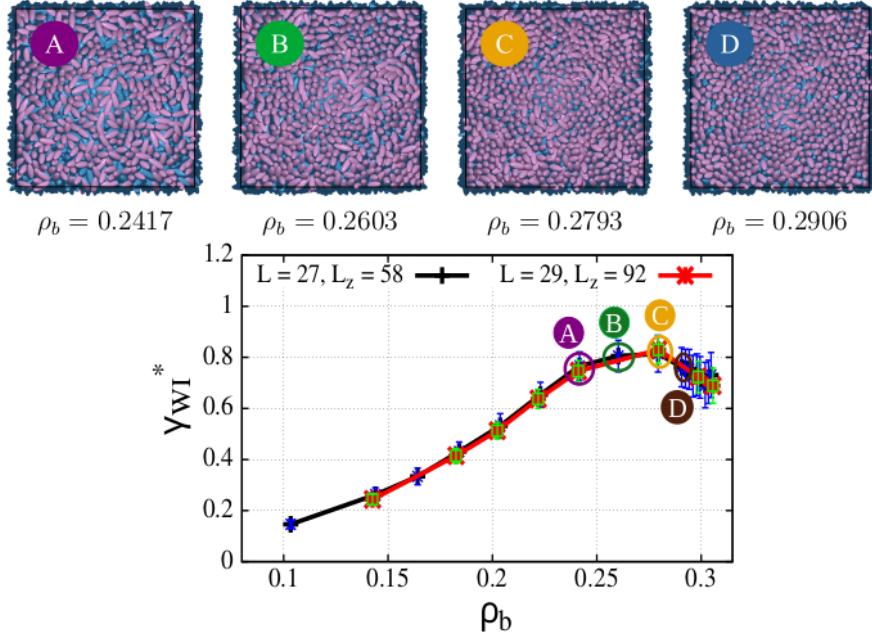


Figure 4.8: The variation of reduced interfacial tension, γ_{WI}^* with bulk number densities (ρ_b) is shown with error bars for two system sizes for $\epsilon_W = \epsilon_0$. The snapshots shown here are the xy -view of the smaller system size near the wall

Earlier studies reveal that the WCA wall-particle interaction strength can be used as a control parameter to modify the interfacial tension [201]. 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 way in which the WCA potential ((2.22)) varies for these four potential strengths (as shown in the inset of Fig. 4.9), there is a similar variation in the interfacial tension with ϵ_W . In other words, the higher the value of ϵ_W , the higher is the γ_{WI}^* . With the increase in the strength of WCA potential (ϵ_W), γ_{WI}^* increases 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 which

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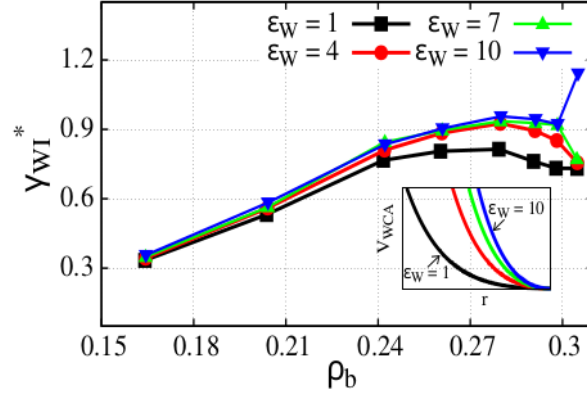


Figure 4.9: The reduced wall-isotropic interfacial tension (γ_{WI}^*) versus bulk number density (ρ_b) for four WCA wall strengths (ϵ_W in units of ϵ_0) for $L = 27.9841$, and $L_z = 58.2131$ system size. The error bars are not shown here as they are similar to those shown in Fig. 4.8. The inset shows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

resulted in a significant rise in P_N , P_T and γ_{WI}^* with ϵ_W . We can see a regular trend in the variation of interfacial tension (γ_{WI}^*) with ϵ_W except at $\rho_b = 0.3047$ and $\epsilon_W = 10$. We believe that such an outlier data point for the 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. Hence, it probably indicates the limitations of the pressure tensor method in calculating the interfacial tension at such a high density where the system is about to acquire nematic order. Secondly, the strength of the wall potential ($\epsilon_W = 10$) in this case might be too high for the stability of the simulations at such high density. The resulting data for the smaller system size is provided in the Table 4.1. In literature, there are various studies of calculating the surface and interfacial tension for different model systems. Here, we have provided a few literature in the Table 4.2

Table 4.1: Data for a system size $L = 27.9841$ and $L_z = 58.2131$ with GB ellipsoids of aspect ratio $= \sigma_{ee}/\sigma_{ss} = 3$ confined between two smooth and soft repulsive WCA walls obtained from MD-NVT simulation⁷⁷. 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
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

SECTION 4.2: RESULTS AND DISCUSSION

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, 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 with 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 $L/\sigma = 1$	[304]
	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	[237]
			$\gamma_{WI}^* = \beta \gamma_{WI} D^2 = 0.0590 \pm 0.0018$ for overall $\eta = 0.1020$	[305]
	Hard walls	Hard spheroplatelets (radius, a)	$\gamma_{WI} = \beta \gamma a^2 = 0$ to 0.05 for $\eta_b = 0$ to 0.48	[306]
		Hard rods	$\beta \gamma_{WI} L D = 0.05$ to 0.07 for $c_I - c_b = 10^{-8}$ to 10^{-2}	[276]
			$\gamma_{WI}^* = \beta \gamma_{WI} D^2 = 0.02$ to 0.006 for $L/D = 10$ to 20	[307]
		Rodlike molecules (for $H/L = 3$ where H is separation b/w walls)	$\gamma^* = 2.24$ to 2.36 for reduced chemical potential $\beta \mu = 7.6$ to 7.8	[308]

		Polymer	$\gamma_{WP}/\gamma_W^{id} = 1$ to 6 (γ_W^{id} is for ideal polymer) for $\rho/\rho' = 0$ to 10	[309]
	Slitlike pore	Hard spherocylinders (L/D = 3.7)	$\gamma_{WI}^* = \beta\gamma_{WI}D^2 = -4.1036$	[310]
	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	[311]
	WCA	GB (3, 5, 2, 1)	$\gamma_{WI}^* = \gamma_{WIV_m}/(\eta_b\sigma_{ee}k_bT) = 0$ 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	[201]
		Asakura-Oosawa (colloid-polymer mixture)	$\beta\gamma_{WF}\sigma^2 = 1$ to 2 for $\eta_b = 0.4$ to 0.5	[202]
Immersed in solution	CTAB solution	Nematic 5CB	$\gamma_{WF} = 5.5$ to 7.5 for temperature = 27 to 41 °C	[312]
	Aqueous SDS solution	5CB	$\gamma = 10$ to 30 mN/m for SDS concentration = 0.01 to 6 mM	[313]
No confinement	Nematic-vapor interface for GB (3, 1, 2, 1)		$\gamma^* = \gamma\sigma_0^2/\epsilon_0 = 0.369$ at $T^* = 0.59$	[240]
	Nematic-isotropic interface for soft rods (L/D = 10)		$\gamma_{IN} = 0.49k_B T/L^2 = 0.0049k_B T/D^2$ for $\beta\epsilon = 2$	[88]
	nCB LCs		surface tension = 29 to 36.5 dynes/cm for $T - T_{NI} = -20$ to 20 K	[314]

4.3 Summary and conclusion

In this chapter, the effects of confining WCA (Eq. (2.22)) walls on GB (Eq. (2.17)) isotropic fluid are presented for a wide range of number densities. Using the simulation snapshots, the 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 have any considerable effect on the bulk isotropic phase. However, as density increases, the wall influences its nearby particles to acquire the positional and/or orientational order. As a result, 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, 4.6, and 4.7). Due to the development of an ordered phase near the walls, the transverse pressure profile ($P_T(z)$) shows oscillations near the walls which further increase as ρ increases (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 ρ_b (Fig. 4.3).

The main aim of this work is to calculate WCA wall-isotropic interfacial tension γ_{WI}^* 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, further increase in ρ induces further wetting of the wall and reduces the interfacial tension. To analyze the finite-size effects, two system sizes with $L \approx L_z/2$ and $L \approx L_z/3$ are simulated, but no significant dependence of γ_{WI}^* on the system sizes, we considered, is observed. 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 is 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 the increasing agitation among the particles with increase in ρ_b and ϵ_W , and

thus 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. The understanding of 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 towards understanding the heterogeneous nucleation and wetting phenomenon 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 [259][27][315] and theoretical calculations [316][8][28]. However, the nucleation phenomenon in materials composed of aspherical particles gives rise to more interesting interfacial properties. For a system containing the rod-like particles, the droplet nucleation for various coexisting phases such as the isotropic-nematic [14], isotropic-smectic [68], isotropic-crystal [59] etc. has been widely studied. There are also studies of nucleation in mixtures containing liquid crystals such as hard rods in hard spheres [317], Gay-Berne particles in Lennard-Jones (LJ) solvent [52], ⁵⁹suspension of colloidal rods and non-adsorbing polymers [318], and so on. In suspensions, the small-sized droplets do not remain stable for a long time, and they aggregate into a single large droplet [52]. Different droplet shapes such as the nematic droplets in the form of tactoids, the formation of smectic phases induced by the surface of metastable nematic droplets, and the smectic membranes in the form of twisted ribbons have been observed in the two components system [318]. Ex-

perimental studies also revealed the generation of nematic ellipsoidal tactoids with rods aligned along the major axis of droplets [24, 62, 319]. The droplet elongation along the particles' director has been observed in various other studies [63, 52, 62]. The ²Gay-Berne (GB) model is the most commonly used model among various LC model systems to simulate liquid crystalline particles. In most of the studies for constrained [294, 140] and unconstrained [55] 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 [55], by changing the molecular elongation [320] and energy anisotropy parameter [321]. For the disc-like GB molecules, the nucleating droplets of different shapes such as sphere or ellipsoid, disk-like [322], lens-like [321] and tactoids with different director field configurations [323] have been observed.

In this chapter, we are presenting our study to investigate the possible shapes of the nematic (nm) and smectic-B (smB) droplets formed during the nematic-smectic B (nm-smB) coexistence. The GB liquid crystalline molecules with (3, 5, 2, 1) set of GB parameters are simulated in a finite cuboidal box at different nm-smB coexisting densities. To analyze the possible shapes of nm or 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 [69]: (a) By calculating $\vec{q}_6 \cdot \vec{q}_6$ [324] 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 ¹²number of nearest neighbor bonds forming a straight line (i.e., pairs lying opposite to each other) for each particle such that the particles with ¹²five or more pairs of bonds forming an angle between 165° and 195° were considered as solid-like ²particles. In a system with rod-like particles, the crystalline phase has been identified from an isotropic liquid phase using a ⁸crystallinity criterion. 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 [67]. In our recent work with GB (3, 5, 2,

1) potential (presented in Chapter 3), we investigated the planar nm-smB interface and the phases were identified by using local bond order parameter, q_6q_6 . There, we determined the nm-smB interfacial energy and coexisting density range [325]. Here, we are showing the morphology of equilibrated nm-smB interfaces within the nm-smB coexistence. Apart from the interest in the 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 [326]. Even, the small sized LC droplets (nanodroplets) has biosensor applications [327].

5.2 Simulation details

The simulations for the GB liquid crystalline system are performed by using the open-source LAMMPS (Large Atomic/Molecular Massively Parallel Simulator) package. All the simulations are performed using the canonical ensemble at temperature, $T = 1$ with MD time step 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., $L = L_x = L_y = L_z$), having periodic boundary conditions applied in all directions and containing GB ellipsoids of unit masses. The diameters of GB ellipsoids along three body-axes are $\sigma_x = \sigma_y = \sigma_0$ and $\sigma_z = 3\sigma_0$. In order to achieve the nm-smB phase coexistence, we have used a *three-step recipe* to simulate the system. The first of the 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 chosen randomly. The system is then simulated for 2×10^6 MD time steps under N_0pT -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_0VT -ensemble, for 2×10^6 MD time steps to equilibrate the system further 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. To accomplish this, two different paths are followed depending on whether ρ is closer ⁴⁰ to the lower (ρ_{nm}^f) or upper (ρ_{sm}^m) end of the nm-smB coexistence range. To have a system with ρ close to ρ_{nm}^f , some particles are deleted randomly from the system barring a central cuboidal part of the simulation box. However, for systems with ρ close to ρ_{sm}^m , the particles are deleted only ⁹ 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 cuboidal part is kept 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 $N = N_0 - N_d$ ⁵ 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 where 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 for 10^7 MD time steps each. In the third step, the data are collected after every 100 MD steps during the run of 10^4 MD times teps. Therefore, all the calculations presented in this report are from these 100 equilibrated configurations.

Simulating the GB LC system is time-consuming primarily owing ²⁸ to the awfully complicated form of the GB potential (Eq. 2.17). ²⁸ The situation is compounded by the fact that capturing the true behavior of the coexistence and nucleation of phases is generally inhibited by the finite system size chosen for the 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 ³²⁸. Our simulation recipe includes several steps (as discussed above). First is the process of getting a well equilibrated, highly dense phase (like a smectic-B phase). This step generally takes around 4 million MD steps and would generally cost three days of simulation time. Next comes the step where the simulation is run for the longest time to get the co-existing 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 time steps	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 the GB parameters (3, 5, 2, 1), the nm-smB coexisting density range is $0.3340 \pm 0.002 < \rho_{co} < 0.3600 \pm 0.002$, where the density for pure nm and smB phases are $\rho_{nm}^f = 0.3340 \pm 0.002$ and $\rho_{sm}^m = 0.3600 \pm 0.002$, respectively [325]. Note that, the droplets appear immediately as ρ exceeds ρ_{nm}^f in the thermodynamic limit but not in the case of finite box [329, 242]. In the thermodynamic limit, the phase coexistence persists within the whole coexistence region and, the stability of droplet is not affected by any kind of boundary conditions. On the other hand, the droplet formation or dissolution is influenced by the boundary effects in finite system size. Therefore, the coexisting density range might get shortened than that in the thermodynamic limit. In order 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 an accurate analysis of the droplets formed.

5.3.1 Phase identification with a sub-box technique

After achieving the equilibrium configurations of 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 [325] (presented in Chapter 3), we have 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 in the present work of scrutinizing the possible shapes of nm and smB droplets formed during their coexistence. However, it turns out that q_6q_6 could only identify the nm-smB planar interface but not the non-planar interfaces formed by aspherical nm and smB droplets. Hence, we took an alternative route for the identification strategy that is 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 the system director. Now, this parameter is an averaged quantity of the particles' orientations. So, we calculated the orientational order in the local environment by dividing the simulation box into small regions, which we call as sub-boxes. Thus, we have used a coarse-grained phase identification technique by calculating the orientational order in sub-boxes, i.e., S_{sb} . Now, for sensible calculation of S_{sb} , the size of the sub-boxes needs to be chosen carefully. This is achieved by plotting the orientational order distributions for different sub-boxing scale and we looked for a well-behaved S_{sb} distributions. Hence, after several trials, the sub-box scaling is chosen to be around 5, which results in well-behaved orientational order distributions (as shown in Figs. [5.1] and [5.2], respectively). Apart from the coarse-grained 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 or smB droplets formed. Therefore in our present work, we have used the S_{sb} distribution to identify the nm and smB phases and their coexistence. To accomplish this, the simulation box is divided into $11 \times 11 \times 11$ sub-boxes of dimensions $5.044733 \times 5.044733 \times 5.044733$

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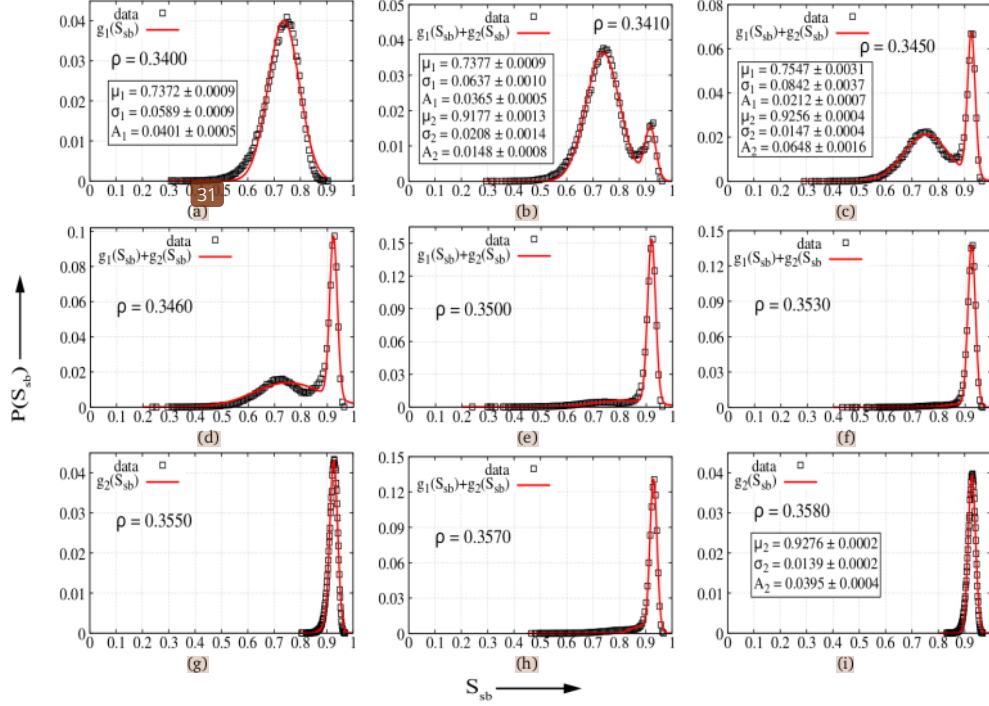


Figure 5.1: The plots of the orientational order distributions at different number densities for smaller system size, i.e., $L = 55.4921$. The orientational order (S_{sb}), plotted along the horizontal axis, is calculated by using the sub-box technique. The symbols (black squares) indicate the data points,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

in x , y and z directions for smaller system size and $19 \times 19 \times 19$ sub-boxes of dimensions $5.115556 \times 5.115556 \times 5.115556$ in x , y and z directions for larger system size. Then, the orientational order is calculated in each sub-boxes 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 are indicating 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 phase (Figs. 5.1(i) and 5.2(i)) is formed without any coexistence then these distributions show only one peak at around $S_{sb} \approx 0.75$

and $S_{sb} \approx 0.92$ for nm and smB phases, respectively. Therefore, in the coexistence, we could safely assume that the sub-boxes having the S_{sb} values less than 0.8 indicate the nm phase, and the sub-boxes having S_{sb} values greater than 0.9 contain the smB phase.

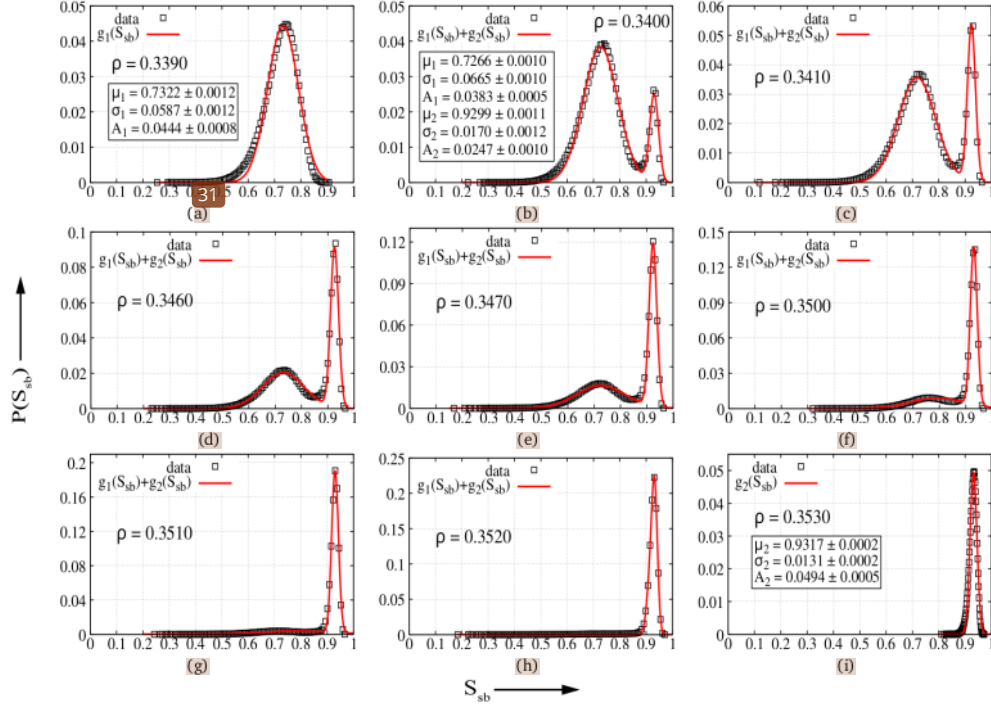


Figure 5.2: The plots of the orientational order distributions at different number densities for larger system size, i.e., $L = 97.1956$. The orientational order (S_{sb}) plotted along the horizontal axis is calculated by using the sub-box technique. The symbols (black squares) indicate the data points, and the line (red-colored) represents the Gaussian fitting curve; $g_1(S_{sb})$ is the gaussian distribution for the nematic peak and $g_2(S_{sb})$ is for the smectic peak. The errors in μ , σ , and A for both the nematic and smectic Gaussian fitting curves are also given for 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 $S_{sb} \geq 0.9$ 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 including the nematic phase, the smectic phase and the 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 the nematic droplet (i.e.,

SECTION 5.3: RESULTS AND DISCUSSION

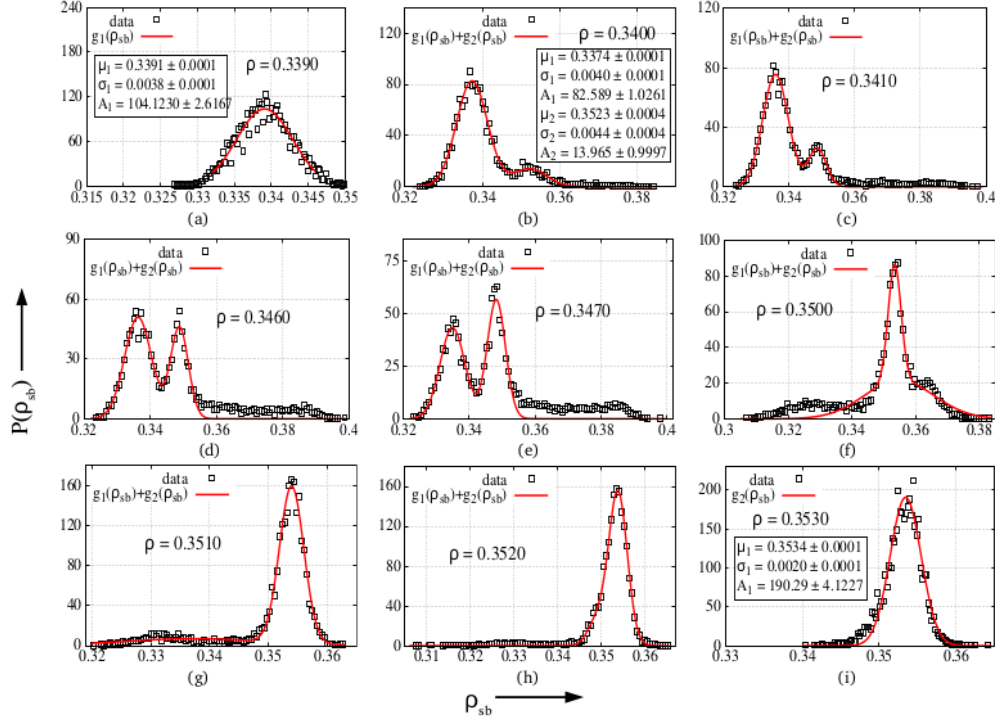


Figure 5.3: The plots of number density distributions at different number densities for larger system size, i.e., $L = 97.1956$. The number density (ρ_{sb}), plotted along the horizontal axis, is calculated by using the sub-box technique. The symbols (black squares) indicate the data points, and the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

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, we are showing the planar-view (i.e., xy or yz or xz) of the droplet formed for a better view of the droplet phase. In these images, the particles in the nm-like and smB-like sub-boxes are colored in blue and pink, respectively. Whereas, the green colored boxes in the top rows of Figs. 5.4, 5.6, 5.7, and 5.8 represent the nm-smB interface, and are the sub-boxes having the intermediate values of S_{sb} (i.e. $0.8 \leq S_{sb} < 0.9$). 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 the best of our knowledge, such a criterion of using a sub-box orientational order parameter is novel and useful to

differentiate between the coexisting nm and smB phases separated by planar and non-planar interfaces. It is to ¹²⁷be noted that because this is a coarse-grained method, so it is not suitable to see any droplet of microscopic size (say consisting of only a few GB molecules).

5.3.2 Shapes of nm and smB droplets

To investigate the different possible shapes of nm and smB droplets, we begin with the nematic density of $\rho_{nm}^f = 0.3340$, that is the lower end of the nm-smB coexistence [325]. 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 starting of Sec. 5.3), it is expected that in the thermodynamic limit, smB droplet would form in a system with density just above $\rho_{nm}^f = 0.3340$. So, the fact that we did not see any droplet here up to density $\rho = 0.3400$, could be due to the following two reasons. Firstly, due to the finite system size effects [329][242] and secondly, the coarse-grained method of calculating the orientational order in sub-boxes S_{sb} could not identify the small droplets formed for $0.3340 \leq \rho \leq 0.3400$. However, we have indeed found the green-colored sub-boxes (Fig. 5.4(a)) representing the nm-smB interface. Therefore, the shortcoming of our sub-boxing identification technique is that sometimes it may miss out on identifying the microscopic-sized droplets in the system. To illustrate this, we have shown the three possible droplet scenarios (in Fig. 5.5), which 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 phase. In the second 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 coarse-grained identification technique.

SECTION 5.3: RESULTS AND DISCUSSION

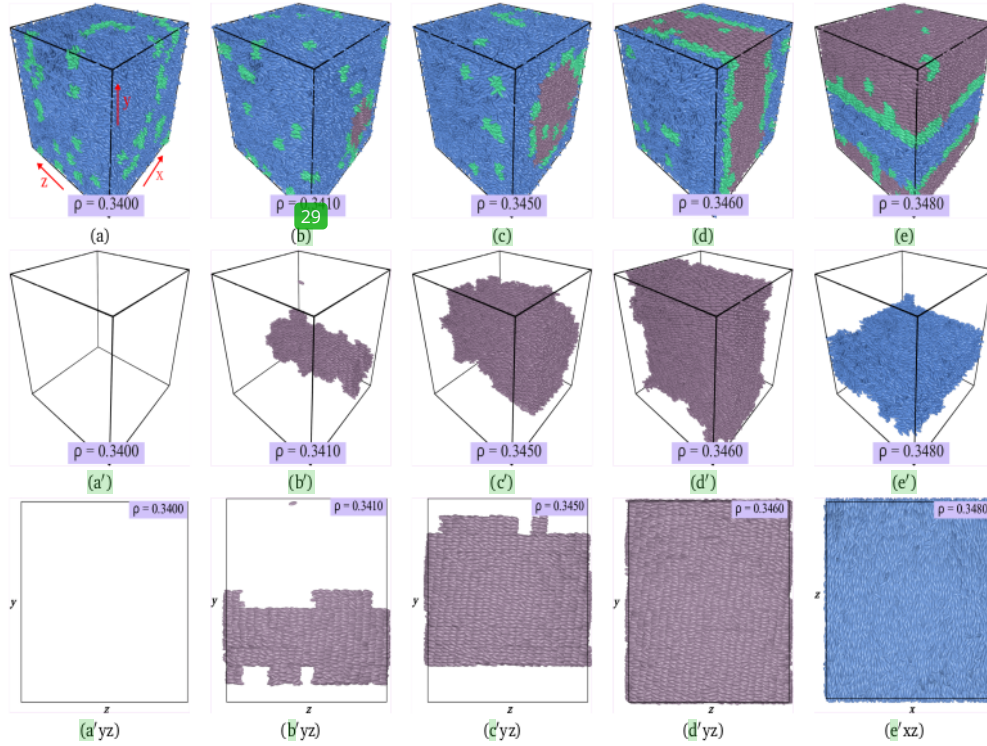


Figure 5.4: The snapshots exhibiting the whole system and the droplet without the interface at different viewing angles at lower nm-smB coexisting number densities for smaller system size, $L = 55.4921$. The nematic phase, smectic-B phase, and the nm-smB interface are represented in blue, pink, and green colors, respectively. Here in a column, the images in the top row represent the whole system (including 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') is showing only the droplet formed in the system shown in (a). In the third row, the planar view of droplets is shown for the better view of the droplet phase. The labeling of the third row images includes the plane-of-view and the prime symbol to signify that only droplet is shown. For instance, the image label (a'yz) indicates that only droplet formed in the system shown in (a) is viewing with the yz -plane-of-view

At $\rho = 0.3410$ (Figs. 5.4(b), 5.4(b'), and 5.4(b'yz)), a cylindrical smB droplet is emerged from the surrounding nm phase. However, in the solid-liquid coexistence for spherical particles, the spherical, cylindrical and planar (slab-like) droplets were found [329, 10]. Therefore, one would expect the sequence of the droplet morphologies in LCs upon increasing number density to be aspherical, cylindrical, and planar.

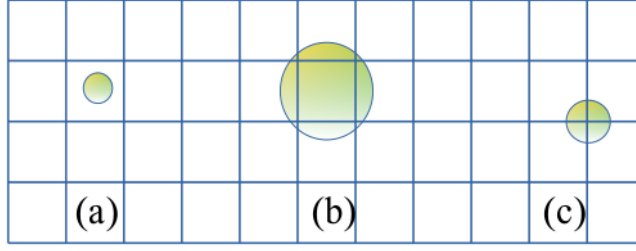


Figure 5.5: A cartoon picture showing the different scenarios of a microscopic droplet formed in a coarse-grained simulation box divided into sub-boxes.

However, our simulation results indicate that the smectic aspherical cluster formed by ellipsoids of 3 aspect ratio is not stable for the number density and system size taken. It might be due to two reasons. One might be due to the similar direction of nm and smB directors. There is an experimental evidence that the orientational order dominates the phase separation more than the translational order [330]. However, in the case of nm-smB coexistence, there is no large difference in the orientational order between the two phases. Therefore for the system size taken, the smB aspherical droplet does not remain stable, 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. In order 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 with the width of smB phase continuously increasing 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 a cost of the nm phase at higher densities. Consequently, the nm droplet was expected to follow a similar but reverse trajectory at higher densities as observed for the smB

SECTION 5.3: RESULTS AND DISCUSSION

droplet at lower densities (i.e., from slab to cylindrical to no droplet). Therefore, after the planar nm-smB interface, a cylindrical nm droplet is observed in the smB phase for $0.3500 \leq \rho \leq 0.3520$ (Figs. 5.6(a), 5.6(a') and 5.6(a'yz)). However, at $\rho = 0.3530$, a nm aspherical cluster surrounded by the smB phase is obtained (see 18 Figs. 5.6(b), 5.6(b') and 5.6(b'yz)). Therefore, unlike the smB droplet, an aspherical nm cluster can be stable in the smB phase. We believe that the stability of such an nm droplet within the smB phase could be due to higher surrounding pressure by the highly ordered smB phase on the less ordered nm droplet. Upon further increasing 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)) with no nm droplet 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 here that the elongation axis of the aspherical nm and smB droplets is found to be along the nematic or smectic-director (Fig. 5.4), which has been observed in various studies [55, 320, 52]. The cluster elongation along the preferred direction occurs to enhance their preferred interface surface area [20]. Also, from the images (Fig. 5.4), 47 the nm and smB directors are found to be nearly parallel to each other for all densities.

Several observations from the simulations of the smaller 121 system size indicate the relevance of incorporating the system-size effects in the 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 droplet is observed at $\rho = 0.3550$, which could be due to our coarse-grained 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. Because 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

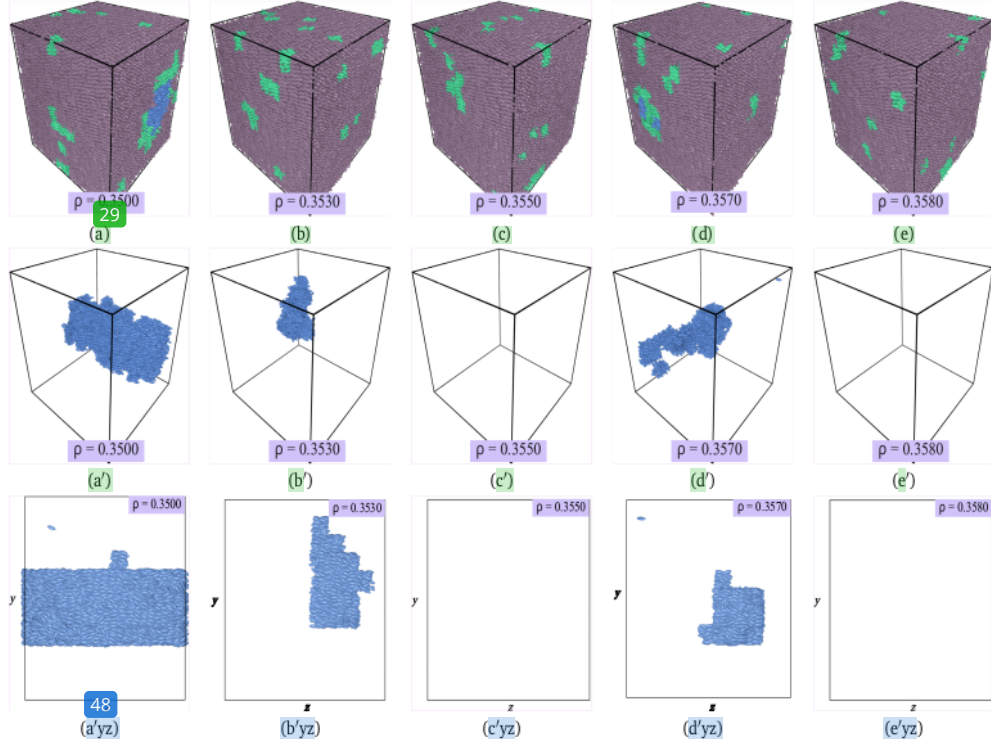


Figure 5.6: The snapshots exhibiting the whole system and droplet without the interface at different viewing angles at higher nm-smB coexisting number densities for smaller system size. Other description of the images are same as in Fig. 5.4.

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 the droplets, due to finite-size effects, indicates the importance of thermodynamic limit for nucleation studies. Hence, we have also simulated a larger system size with $L = 97.1956$.

For the larger system size, the simulations begin with $\rho_{nm}^f = 0.3340$. No smB droplet is found for $\rho \leq 0.3390$ and the whole system is occupied by the nm phase (Figs. 5.7(a), and 5.7(a')). As discussed earlier, it could be due to the finite system size or the coarse-grained 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,

SECTION 5.3: RESULTS AND DISCUSSION

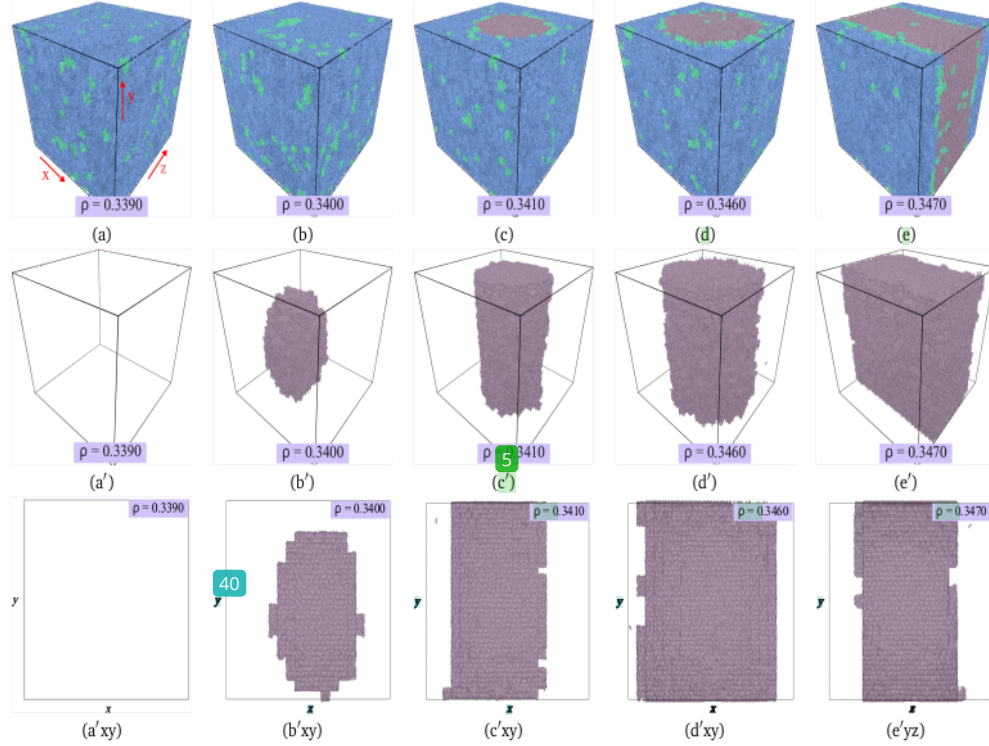


Figure 5.7: The snapshots exhibiting the whole system and droplet without the interface at different viewing angles at lower nm-smB coexisting number densities for larger system size, $L = 97.1956$. Other description of the images are same as in Fig. 5.4

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 is increasing with ρ (Figs. 5.7(c'), and 5.7(d')). Further, for $0.3470 \leq \rho \leq 0.3500$, the planar nm-smB 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)). Afterwards, the cylindrical nm droplet and an aspherical nm cluster are appeared at $\rho = 0.3510$ and $\rho = 0.3520$, respectively (Fig. 5.8(c), and 5.8(d)). This 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 the aspherical droplets is found to be along the nm or smB-director, as

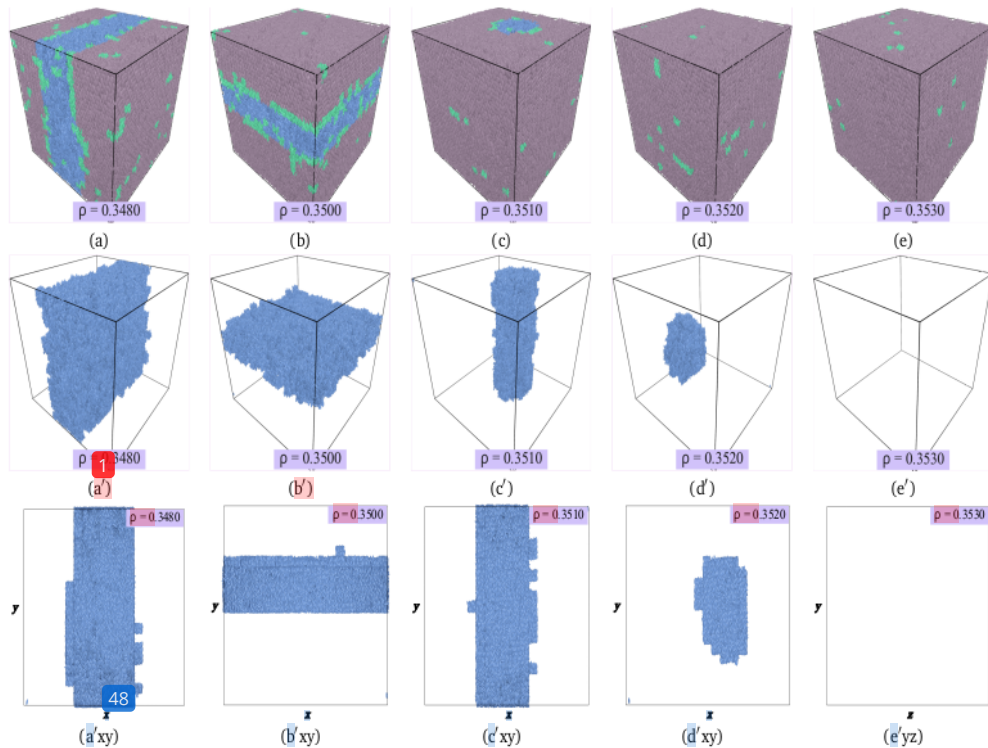


Figure 5.8: The snapshots exhibiting the whole system and droplet without the interface at different viewing angles at higher nm-smB coexisting number densities for larger system size, $L = 97.1956$. Other description of the images are same as in Fig. 5.4

is observed for the smaller system size. Also, the ⁴nm and smB directors are nearly parallel for all densities. To sum up, the Gay-Berne nm and smB phases can coexist with each other, separated by aspherical, cylindrical, and planar interfaces within the nm-smB coexistence region.

42 5.4 Summary and conclusion

In this chapter, a comprehensive study of morphologies of nm or smB droplets formed within the nematic-smectic B coexistence region is presented. The nm-smB phase coexistence is obtained by using our *three-step recipe* (sec. 5.2). Then, we found that identifying the nm or smB droplets formed in the nm-smB phase coexistence

SECTION 5.4: SUMMARY AND CONCLUSION

is not straightforward. First, we used a particle-based identification strategy (using q_6q_6) to distinguish between the 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 [325] 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 novel coarse-grained 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 having 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

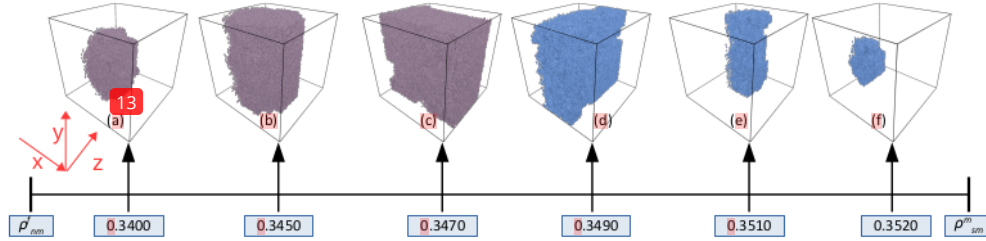


Figure 5.9: One-dimensional morphology diagram along the nm-smB phase coexistence line for GB LC material. As the overall density (ρ) of the system is increased from $\rho_{nm}^f = 0.3340$ to halfway within the nm-smB coexistence region, the smB droplet surrounded by the nm phase changes its shape as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

different system sizes gave 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 such that the more ordered smB phase grows and results in a cylindrical droplet in 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 to grow through the more ordered smB phase. In contrast, for the larger system size, both the aspherical nm droplet inside the smB phase and the aspherical smB droplet within the nm phase are observed. 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 aspherical droplets formed is found to be nearly parallel to the nm and smB directors, which has been observed in various studies for the isotropic-nematic phase transition [24, 62, 319]. Finally, the 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 within the nm-smB coexistence. Understanding such an interfacial phenomenon is crucial due to their various industrial applications, such as biosensors, functional materials, etc.

Chapter 6

Summary and concluding remarks

This thesis is presenting the study of interfacial phenomenon in liquid crystalline material using the ³ molecular dynamics simulations 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) set of GB parameters. The phase-coexistence in a system of GB particles has been examined with and without confinement. In the case of an unconfined GB system, the stiffness of an interface between nematic (nm) and smectic-B (smB) phases has been computed using the capillary wave theory (as described in Chapter 3). Using the density profiles across the interface, the range of nm-smB coexisting densities has been calculated as $\rho_{nm}^f = 0.334 \pm 0.002 < \rho_{co} < \rho_{sm}^m = 0.360 \pm 0.002$. This important finding fulfills the first objective of this thesis. The coexisting nm and smB phases separated by a planar interface are identified by using a particle-based (microscopic) local bond order parameter (i.e., $q_6 q_6$). The directors of nm and smB phases are found to be ⁴ nearly parallel to each other and perpendicular to the interface normal. The nm-smB planar interface is found to be a rough, and is anticipated due to the small aspect ratio (i.e., $\kappa = 3$) of the GB ellipsoids. Using the CWT analysis, the interfacial stiffness of the nm-smB interface comes out to be $\tilde{\gamma}_{nm-smB} = 0.39861 k_B T / \sigma_{ee}^2 = 0.04429 / \sigma_{ss}^2$ 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 system (with longer GB ellipsoids) would be tough to achieve. Furthermore, the nm-smB interfacial properties with non-planar anchoring also need to be explored.

⁹In addition to the unconfined GB system, the interfacial tension of the GB LCs confined by two soft-smooth-repulsive WCA walls has also been determined, as discussed in Chapter 4. By observing the simulation snapshots, pressure tensor profiles, and orientational order parameter near the walls, we found that at lower densities, the mechanical anisotropy introduced by the WCA walls to the system is very small and hence the interfacial tension of wall-isotropic GB fluid interface is low. 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 order of the homeotropic alignment near the wall increases 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). Then, ⁴using the pressure-tensor method, the interfacial tension γ_{WI}^* of an interface between the GB isotropic fluid and the WCA wall is determined. The 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 present near the wall induce further wetting, reducing the energy required to form an interface. Moreover, the finite-size effects are analyzed and no significant dependence of γ_{WI}^* on the system sizes, we considered, is observed. The γ_{WI}^* is found to be dependent on wall-particle interaction strength ϵ_W (Fig. 4.9), such that the higher the ϵ_W , the higher is the γ_{WI}^* . With an increase in ϵ_W , the γ_{WI}^* increases till the density close to the ¹⁰isotropic-nematic phase transition density. At further higher densities, γ_{WI}^* reduces, possibly due to increased agitation between the particles. A thorough analysis of bulk behavior at higher densities, including the isotropic-nematic phase transition density, is still required. Therefore, the fluid confined by WCA walls at and above the isotropic-to-¹⁰nematic phase transition density can be

further investigated. Moreover, **the** interfacial properties of confined GB systems with higher aspect ratio of ellipsoids and walls having different properties, like wall-particle interaction potential, microscopic structures, can also be investigated. Thus, the findings described above regarding the properties of nm-smB and wall-isotropic interfaces of GB LC material addresses the second objective of this thesis.

We have also studied the morphology of the GB nematic (nm) or smectic-B (smB) droplets formed within the nm-smB phase coexistence (as discussed in Chapter 5). The nm-smB phase coexistence is achieved by using a *three-step recipe* (refer sec. 5.2). The identification of coexisting nm and smB phases is done by developing a novel coarse-grained identification 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 further confirm the nm-smB phase coexistence (Figs. 5.1 and 5.2). Using these distributions, an identification criterion is developed, such as the sub-boxes with $S_{sb} < 0.8$ have the nm phase, and the sub-boxes having $S_{sb} \geq 0.9$ contain the smB phase. The sub-boxes with intermediate values, such as $0.8 \geq S_{sb} > 0.9$, represent the nm-smB interface. Therefore, using the sub-box orientational order criterion, we have found the aspherical, cylindrical, and planar shapes of nm and smB droplets formed within the coexistence (shown in Figs. 5.4, 5.6, 5.7 and 5.8). As a result, the coarse-grained identification technique has successfully distinguished between nm and smB phases and provided a rough view of the shapes of droplets formed within the nm-smB phase coexistence. However, the true behaviour of coexistence can only be captured at thermodynamic limit, so to address this we have also analyzed our simulation data for two different system sizes. Several observations made with smaller system sizes are found to differ from those of the larger system size. Consequently, these results indicate the relevance of including the finite-size effects for the better understanding of the interfacial phenomenon. For both the system sizes, the elongation of aspherical droplets is found to be nearly parallel to nm and smB directors. These results regarding the homogeneous nm-smB droplet morphologies fulfill the third objective of this thesis. This work can be further extended by calculating the chem-

ical potential and the free energy difference required for stabilizing the nm and smB droplets. Moreover, ⁶⁶ the effect of the aspect ratio on the droplet morphology would also be interesting to check. Apart from pure academic interest regarding the nucleation phenomenon in LC materials, understanding of such interfacial phenomenon is crucial for better processing of LC materials and due to their various industrial applications, as in biosensors, functional materials, etc.

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