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**The importance of the shape
effect in phases with
non-standard symmetries: a
hard-particle Monte Carlo study**

Doctoral Thesis

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Abstract

Liquid crystals (LCs) are a mesophase that combines the properties of liquids and solids. They are commonly found in nature and are a basis of liquid-crystal display (LCD) technology. The nematics are a type of LCs, where the system's density is uniform. However, the molecules orient in a preferred direction. Since their discovery in 1888 by Reinitzer, further four subsequent generations of nematics were experimentally identified, each time opening new possibilities and finding new applications. The two most recent generations observed in the 21st century, including phases such as twist-bend (N_{TB}), splay (N_S), and ferroelectric (N_F) nematics, are the subject of ongoing scientific debate. While new classes of molecules forming them are synthesized by the experimentalists, the theorists discuss the molecular factors that stabilize them. Greco and Ferrarini [2015 *Phys. Rev. Lett.* **115**(14) 147801] showed that purely entropic interactions are enough to promote twist-bend modulation in bent-core systems, which was further confirmed by different computational studies. On the other hand, the origin of N_S and N_F is still being discussed. The two most important factors appear to be a conical shape and a large dipole moment of a molecule.

This Thesis, which treats purely hard-core particles via Monte Carlo simulations, aims to expand the understanding of the shape effect in N_{TB} systems and determine their stability under varied parameters, as well as assess the possibility of obtaining N_S and N_F phases without the help of dipolar interactions. It was established that the N_{TB} phase is quite resilient to modifications in the shape of the particles. However, long-range polarization and splay order in hard-core conical systems were observed only for crystalline phases, while for liquids, they were at most local. The Thesis is based on five scientific articles, among which four have already been published. Before providing their short summary, it gives a theoretical background of the problems in question, as well as discusses simulation techniques and an original RAMPACK simulation package that has been developed for the last four years.

Streszczenie

Ciekłe kryształy (CK) to mezofaza, która łączy właściwości cieczy i ciał stałych. Są one powszechnie obecne w przyrodzie i stanowią podstawę technologii wyświetlaczy ciekłokrystalicznych (ang. *liquid-crystal display* – LCD). Nematyki są rodzajem CK, w których gęstość układu jest jednorodna, ale cząsteczki orientują się w preferowanym kierunku. Od ich odkrycia w 1888 roku przez Reinitzera, kolejne cztery generacje nematyków zostały zidentyfikowane eksperymentalnie, za każdym razem otwierając nowe możliwości i znajdując nowe zastosowania. Dwie najnowsze generacje zaobserwowane w XXI wieku, obejmujące fazy takie jak nematyk twist-bend (N_{TB}), nematyk splay (N_S) i nematyk ferroelektryczny (N_F), są przedmiotem trwającej debaty naukowej. Podczas gdy nowe klasy cząsteczek, które je tworzą, są syntetyzowane przez eksperymentatorów, teoretycy dyskutują nad czynnikami molekularnymi, które je stabilizują. Greco i Ferrarini [2015 *Phys. Rev. Lett.* **115**(14) 147801] wykazały, że oddziaływania czysto entropowe wystarczają do promowania modulacji typu twist-bend w systemach bent-core, co zostało później potwierdzone przez kolejne badania komputerowe. Z drugiej strony, pochodzenie N_S i N_F wciąż jest dyskutowane. Dwoma najważniejszymi czynnikami wydają się być stożkowaty kształt i duży moment dipolowy cząsteczki.

Niniejsza praca doktorska, obejmująca cząsteczki o wyłącznie twardych oddziaływaniach, poprzez symulacje Monte Carlo, ma na celu poszerzenie zrozumienia efektu kształtu w układach N_{TB} i określenie ich stabilności przy różnicowaniu parametrów, oraz ocenę możliwości uzyskania faz N_S i N_F bez pomocy oddziaływań dipolowych. Stwierdzono, że faza N_{TB} jest stosunkowo odporna na modyfikacje kształtu cząsteczek. Z drugiej strony, w układach stożkowych z wyłącznie twardymi oddziaływaniami, długozasiegową polaryzację i porządek typu splay zaobserwowano dopiero dla faz krystalicznych, podczas gdy dla cieczy było one najwyżej lokalne. Praca opiera się na pięciu artykułach naukowych, spośród których cztery zostały już opublikowane. Przed zaprezentowaniem ich krótkiego podsumowania, przedstawia teoretyczne podstawy postawionych zagadnień, oraz omawia techniki symulacyjne i oryginalny pakiet symulacyjny RAMPACK, który był rozwijany przez ostatnie cztery lata.

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List of Abbreviations

API	A pplication P rogramming I nterface
AST	A bstract S yntax T ree
CI	C ontinuous I ntegration
CLL	C ell L inked L ist
DP	D esign P attern
DS	D ouble S play
DT	D ouble T wist
GPGPU	G enetal-Purpose P rograming on G PU
LC	L iquid C rystal
LCD	L iquid-Crystal D isplay
MC	M onte C arlo
MCMC	M arkov C hain M onte C arlo
MD	M olecular D ynamics
MHA	M etropolis- H astings A lgorithm
MPI	M essage P assing I nterface
NN	N earest N eighbor
OOP	O bject- O riented P rogramming
OZF	O zeen- Z ocher- F runk (energy density)
PBC	P eriodic B oundary C onditions
SIMD	S ingle I nstruction, M ultiple D ata
SMSB	S pontaneous M irror S ymmetry B reaking
SS	S ingle S play
SSB	S pontaneous S ymmetry B reaking
VL	V erlet L ist
WCA	W eeks- C handler- A nderson (potential)

Chapter 1

Introduction

Liquid crystals (LCs) are a state of matter with properties of both liquids and solids [1, 2]. On the one hand, the mass centers of molecules forming LC phases (mesogens) are at least partially disordered, and the phase can retain a flow like a regular liquid. On the other hand, molecular orientations behave differently – they align along a preferred direction called the director [1]. As a result, the LC phase is optically anisotropic, and one observes a whole array of phenomena, such as the presence of optical textures [3], reflection of circularly polarized light, or bending of linearly polarized one [4]. The last phenomenon led to the development of one of the most important technologies in the modern world: liquid crystalline displays (LCDs) [5, 6]. LC phases also appear in nature, for example, within biological matter [7–9].

Historically, the first liquid crystalline phase was cholesteric (N^*), observed in 1888 by Reinitzer for inherently chiral derivatives of cholesterol [10], where the director rotated around the axis perpendicular to it. Consequently, it constitutes the first generation of nematics (LC phases with uniform density). The second generation of nematics are uniaxial nematics ($N_U \equiv N$) with a non-modulated director field. They possess the highest symmetry of all LC types and are the most widely studied, with countless practical applications. In the mid-20th century, the third generation of nematics was observed: the blue phases (BPs) [11]. The structure of BPs is quite complicated, with an ordered or disordered configuration of linear defects in the director field on a length scale of a blue-light wavelength (hence the name). The next, fourth generation of nematics was not discovered until the beginning of the 21st century, when the modulated twist-bent nematic phase (N_{TB}) was experimentally found in a system of banana-shaped mesogens, with the director precessing around the cone [12–15]. Notably, the structure is chiral while the molecules are achiral, which is an example of spontaneous mirror symmetry breaking (SMSB). The fifth generation of nematics was recently discovered [16–23]. Among several new phases, the most important are the splay nematic (N_S) and the ferroelectric nematic (N_F). In the N_F phase, in addition to orientational ordering along the director, a spontaneous nonzero macroscopic polarization is observed, which breaks the up-down symmetry of a standard uniaxial nematic. On the other hand, in N_S , polar domains with splay modulation are formed, but the phase is

globally apolar.

The main goal of this Thesis is to assess the importance of the molecular shape for the self-assembly and stability of the two most recent generations of LC phases by employing hard-particle Monte Carlo computer simulations. The shape effect was already shown not only to explain the formation of a standard uniaxial nematic (the famous Onsager model) but also, recently, Greco and Ferrarini reported the observation of N_{TB} in a purely steric system [24]. The thesis expands upon this approach. In addition to nematic phases, the adjacent smectic and crystalline phases and the relations between them are also of interest. The thesis is based on a series of five articles.

- A.1 Kubala, P., Tomczyk, W., & Cieřla, M. (2022). In silico study of liquid crystalline phases formed by bent-shaped molecules with excluded volume type interactions. *J. Mol. Liq.*, **367**, 120156.
- A.2 Kubala, P., Tomczyk, W. & Cieřla, M. (2024) Relationship between size of bent-shaped molecules and mesophase formation: a computational study. Under review in *J. Mol. Liq.*
- A.3 Kubala, P., & Cieřla, M. (2023). Splay and polar order in a system of hard pear-like molecules: confrontation of Monte Carlo numerical simulations with density functional theory calculations. *Soft Matter*, **19**(40), 7836-7845.
- A.4 Kubala, P., Cieřla, M., & Longa, L. (2023). Splay-induced order in systems of hard tapers. *Phys. Rev. E*, **108**(5), 054701.
- A.5 Kubala, P., & Cieřla, M. (2024). Inderdigitation, double twist, and topological defects in a system of hard lollipops. *Liq. Cryst.*, 1-14.

It is structured as follows: Chapter 2 provides a basic theoretical introduction to LCs. Chapter 3 describes the most relevant LC phases with a nonstandard symmetry. Chapter 4 summarizes the computational Monte Carlo algorithm used throughout the studies. Its implementation within the original open-source RAM-PACK simulation package is presented in Chapter 5. Finally, the articles with a short summary are gathered in Chapter 6.

Chapter 2

Liquid crystals: theory

2.1 Basics

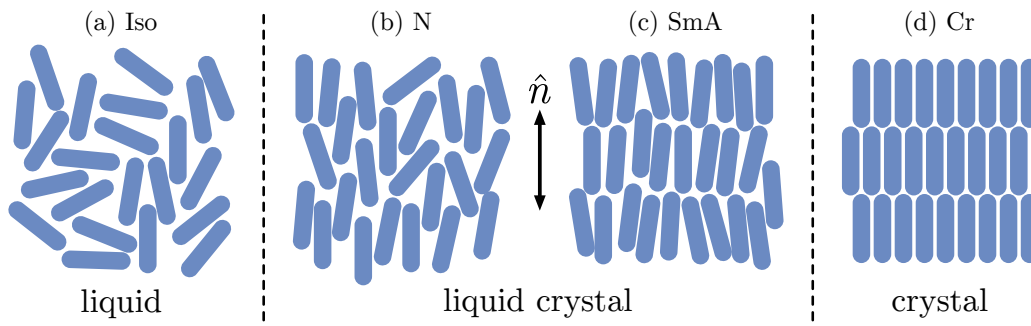


Figure 2.1: Illustration of a common LC phase sequence: Iso-N-SmA-Cr. (a) Isotropic liquid (Iso) – no translational or orientational order; (b) Uniform nematic (N) – no translational order, but molecules prefer alignment parallel to the director $\hat{n}$; (c) type A smectic (SmA) – apart from orientational alignment, one-dimensional translational order appears in the form of periodic layers; (d) crystalline structure (Cr) – there are long-range correlations of both positions and orientations of molecules.

Mesogenic materials form liquid-crystalline phases only in a specific range of thermodynamic parameters. By changing them, one encounters several phase transitions between phases of varying ordering. LCs can be divided into two main types based on a parameter that drives the phase transition. The first and most common type are thermotropic LCs, where the temperature T is a control parameter [1, 25]. For a sufficiently high temperature, the material is a standard isotropic liquid [Iso, see Fig. 2.1(a)] with no orientational or translational order and short-range correlations. Upon cooling, a spontaneous alignment of the orientation of the molecules arises. Typically, the uniaxial nematic is then formed [see Fig. 2.1(b)]. For many standard mesogenic chemical compounds, further cooling results in the formation of another liquid crystalline phase, the smectic Sm [6, 26, 27] [see also Fig. 2.1(c)]. It retains the orientational order of the nematic, but simultaneously, a partial translational order appears in the form of periodic undulation of the local den-

sity ρ . At the same time, molecules can diffuse freely in the whole system, both within the layers and between them. The simplest smectic phase is type A smectic (SmA), where the director is parallel to the wavevector of density modulation, and no additional order is observed in the direction orthogonal to it. Finally, at even lower temperatures, the system undergoes a transition to a crystalline phase [Cr, see Fig. 2.1(d)], where both the positional and orientational orders are fully established. Consequently, a common phase sequence in LC materials is Iso-N-SmA-Cr [1, 26, 28, 29].

Although twist-bend, ferroelectric, and splay nematic LC phases, which are the main topic of the thesis, were experimentally observed in thermotropic systems, it is important to mention the second type of LCs: lyotropic LCs [7, 30]. Instead of the temperature, the driving force is the concentration of the molecules in a solvent. Upon increasing the concentration, the system may undergo a phase sequence similar to that for thermotropic LCs. One often refers to systems with purely hard-core interactions used in computational studies as the lyotropic ones because the phase sequence is analyzed as a function of the packing fraction η^1 , which is an analogue of the concentration. In addition, purely repulsive interactions prove to be a good model for colloidal nanoparticle systems [31], which are essentially lyotropic.

The next sections will focus mainly on the basic Iso-N-SmA-Cr sequence of the LC phase transitions and describe them from three different angles: through order parameters, symmetry breaking, and packing entropy. Finally, the last section introduces the phenomenological Landau and Landau-de Gennes models with an extension to modulated phases.

2.2 Phase transitions I: order parameters

In general, phase transitions are described using the so-called order parameters [1, 32]. They are specific quantities, usually experimentally measurable, whose changes signal a phase transition. The simplest example is the density of water, which shows sharp changes when the water boils or freezes under the normal atmospheric pressure. Typically, order parameters are defined in such a way that they are equal to zero in a disordered phase above the phase transition point and greater than zero for an ordered phase below the transition point. The behavior of order parameters during the phase transition can also distinguish its type. In the first-order phase transitions, the order parameter experiences a sharp, discontinuous jump (as in the above example of water), while in the second-order phase transitions, the change is continuous.

In the context of LCs, the most important order parameters are the nematic order parameter P_2 (sometimes denoted as S), which measures the ordering of orientations, and the smectic order parameter τ that detects density modulations. They are described in the next parts of this section. Two other order parameters – polarization M and bond order ψ – are also introduced, as they are used

¹Packing fraction is defined as $\eta = V_P/V$, where V_P is the total volume of all particles and V is the volume of the enclosing simulation box.

throughout the studies [A.1-5].

As the research mainly involves computer simulations, the order parameters are defined in a computational-friendly way, namely as an average over a finite number N of particles $1/N \sum_{i=1}^N$ and over independent snapshots $\langle \dots \rangle$ of the studied system

$$\langle O \rangle = \left\langle \frac{1}{N} \sum_{i=1}^N O_i \right\rangle. \quad (2.1)$$

Here, O_i is the (local) value of the order parameter O for the i th particle. In the case of the Monte Carlo simulations, averaging over independent system snapshots corresponds to ensemble averaging.

2.2.1 Nematic order

The nematic order parameter P_2 measures the deviation of long molecular axes $\hat{\mathbf{a}}$ from a preferred direction of the system, called the director $\hat{\mathbf{n}}$ [1]. Assuming both $\hat{\mathbf{a}}$ and $\hat{\mathbf{n}}$ are normalized, P_2 is defined as

$$\langle P_2 \rangle = \left\langle \frac{1}{N} \sum_{i=1}^N P_2(\hat{\mathbf{a}} \cdot \hat{\mathbf{n}}) \right\rangle, \quad (2.2)$$

where $P_2(x) = (3/2)x^2 - 1/2$ is the second-order Legendre polynomial [33]. The nematic order parameter is equal to 1 in a perfect uniaxial nematic, falls to 0 for a disordered system, and reaches $-1/2$ when all particles are orthogonal to $\hat{\mathbf{n}}$.

This definition assumes prior knowledge of the director $\hat{\mathbf{n}}$. The Landau-de Gennes $\mathbf{Q}$ -tensor formalism [34, 35] (further discussed later), however, alleviates this issue. For a single snapshot, the $\mathbf{Q}$ -tensor is defined as

$$\mathbf{Q} = \frac{1}{N} \sum_{i=1}^N \frac{3}{2} \left(\hat{\mathbf{a}}_i \otimes \hat{\mathbf{a}}_i - \frac{1}{3} \mathbf{I} \right), \quad (2.3)$$

where $(\mathbf{x} \otimes \mathbf{y})^{ij} = x^i y^j$ is the outer product and $\mathbf{I}$ is the identity matrix. The $\mathbf{Q}$ -tensor is traceless and symmetric. An instantaneous value of the nematic order parameter P_2 is then the eigenvalue of $\mathbf{Q}$ with the highest magnitude, while the corresponding eigenvector is the director $\hat{\mathbf{n}}$. Two other eigenvalue-eigenvector pairs can be used to assess the biaxiality of the $\hat{\mathbf{a}}$ axis field; if the eigenvalues are not equal, the structure is biaxial. To measure biaxiality in a system of particles lacking axial symmetry, two other molecular axes must be incorporated into the $\mathbf{Q}$ -tensor, which is outside of the scope of the thesis. It is important to note that the $\mathbf{Q}$ -tensor formalism reflects well the symmetries of the nematic phases; thus, it is often used in theoretical studies [35–39].

2.2.2 Smectic order

The smectic order parameter τ measures the density modulation in the system [1]. It is defined as

$$\langle \tau \rangle = \left\langle \frac{1}{N} \left| \sum_{i=1}^N \exp(i\mathbf{k} \cdot \mathbf{r}_i) \right| \right\rangle, \quad (2.4)$$

where ι is the imaginary unit, $\mathbf{k}$ is the wavevector of modulations, and $\mathbf{r}_i$ is the mass center of i th particle. Please note that the modulus $|\cdots|$ is computed before ensemble averaging $\langle \cdots \rangle$ to cancel out the collective movement of layers with respect to the lab frame. For a uniform system $\langle \tau \rangle = 0$, while for perfect layers with no spread of mass centers $\langle \tau \rangle = 1$. For sinusoidal modulation of the particles' density $\langle \tau \rangle = 1/2$.

The computation of τ requires a prior assumption of $\mathbf{k}$. Thus, one usually chooses $\mathbf{k}$ giving the highest $\langle \tau \rangle$. In a simulation box, $\mathbf{k}$ must also be compatible (commensurate) with periodic boundary conditions (PCB). The easiest way to enumerate all allowed values is via the Miller indices $h, k, l \in \mathbb{Z}$ [40]

$$\mathbf{k}_{hkl} = h\mathbf{g}_1 + k\mathbf{g}_2 + l\mathbf{g}_3, \quad (2.5)$$

where $\mathbf{g}_i$, $i = 1, 2, 3$ are reciprocal box vectors:

$$\mathbf{g}_1 = \frac{2\pi}{V}(\mathbf{v}_2 \times \mathbf{v}_3), \quad (2.6)$$

$$\mathbf{g}_2 = \frac{2\pi}{V}(\mathbf{v}_3 \times \mathbf{v}_1), \quad (2.7)$$

$$\mathbf{g}_3 = \frac{2\pi}{V}(\mathbf{v}_1 \times \mathbf{v}_2). \quad (2.8)$$

Here, $\mathbf{v}_i$, $i = 1, 2, 3$ are vectors spanning the simulation box and $V = |\mathbf{v}_1 \cdot (\mathbf{v}_2 \times \mathbf{v}_3)|$ is the volume of the box.

2.2.3 Polarization

The standard nematic and smectic phases are apolar. However, as the Thesis discusses nonstandard phases with, at least local, nonzero polarization, it is instrumental to devise an appropriate order parameter. For a globally polar phase, one can simply use the bulk polarization density $\mathbf{P}$ (the volume density of the dipolar moments of molecules) [20]. Alternatively, one can use a normalized parameter based on unit vectors

$$\langle M \rangle = \left\langle \frac{1}{N} \sum_{i=1}^N \hat{\mathbf{b}}_i \cdot \hat{\mathbf{M}} \right\rangle, \quad (2.9)$$

where $\hat{\mathbf{b}}_i$ is the polarization axis of i th molecule and $\hat{\mathbf{M}}$ is the polarization versor (a normalized vector), assumed a priori. The parameter ranges from -1 to 1 , where the extreme values correspond to a perfect (anti)polarization, and 0 is achieved for a disordered system or one with the polarization axes orthogonal to $\hat{\mathbf{M}}$.

Again, one can construct a more general definition with no initial assumptions by averaging the polarization vectors

$$\langle M \rangle = \left\langle \frac{1}{N} \left\| \sum_{i=1}^N \hat{\mathbf{b}}_i \right\| \right\rangle. \quad (2.10)$$

Here, a vector norm $\|\cdots\|$ is computed separately for each snapshot to account for a possible diffusive drift of the polarization vector direction. For such a definition,

$\langle M \rangle$ ranges from 0 to 1 for, respectively, a disordered system and a fully polarized one.

Until that point, only bulk polarization was considered. However, the system may possess a complicated local polarization pattern with zero global polarization. For example, in the twist-bend nematic N_{TB} phase (discussed later), the polarization is constant in a plane perpendicular to the structure wavevector $\mathbf{k}$, but its direction rotates when one moves along it. In such a case, the order parameter can be defined plane-wise (assuming $\mathbf{k} \parallel \hat{\mathbf{z}}$)

$$\langle M \rangle = \left\langle \frac{1}{V} \int dz \left\| \int dx dy \hat{\mathbf{b}}(x, y, z) \right\| \right\rangle \quad (2.11)$$

Other variants include the local polarization order $\langle m \rangle$, which can be computed by averaging $\hat{\mathbf{b}}_i$ over a local neighborhood of a single particle and then averaging its modulus over the whole system and independent system snapshots. Alternatively, as in the study [A.3], instead of taking the average modulus of $\hat{\mathbf{b}}_i$, one can compute the scalar product $\hat{\mathbf{b}}_i \cdot \hat{\mathbf{n}}$ with a local director calculated for the entire neighborhood.

2.2.4 Bond order

Some smectic phases, for example, type B and type I smectics [6] possess a partial translational order within the layers, where the vectors (bonds) joining nearest neighbors (NN) form local hexatic structures with a globally synchronized phase, while the mass centers still lack long-range correlations. For such a system, the so-called bond order parameter Ψ_α is devised [41]. It is defined by projecting the particles onto the nearest layers and then treating each layer as a two-dimensional system:

$$\langle \Psi_\alpha \rangle = \left\langle \frac{1}{N} \left| \sum_{i=1}^N \frac{1}{\alpha} \sum_{j \in \alpha \text{NN}(i)} \exp(\alpha i \theta_{ij}) \right| \right\rangle. \quad (2.12)$$

Here, α is the rank ($\alpha = 4$ for tetratic order, $\alpha = 6$ for hexatic order), $\alpha \text{NN}(i)$ is a set of α nearest neighbors of the i th particle, while θ_{ij} is the angle between the vector joining the i th and j th particle, and an arbitrary but constant direction on a plane. The value ranges from 0 for a disordered system to 1 for a perfect bond alignment. Naturally, $\langle \Psi_\alpha \rangle$ also detects long-range crystalline order.

It is important to note that $\langle \Psi_\alpha \rangle$ in its original form (2.12) may be artificially lowered due to domain formation. One may also want to measure local bond ordering without assessing the global phase. The local bond order parameter can be constructed by exchanging the order of computing the modulus and averaging over the system:

$$\langle \psi_\alpha \rangle = \left\langle \frac{1}{N} \sum_{i=1}^N \frac{1}{\alpha} \left| \sum_{j \in \alpha \text{NN}(i)} \exp(\alpha i \theta_{ij}) \right| \right\rangle. \quad (2.13)$$

Such a variant was used in the studies [A.2-5]. Although the local bond order parameter $\langle \psi_\alpha \rangle$ is not susceptible to the formation of domains, the downside is

that it does not fall to 0 even for a fully disordered system – it is equal $\langle\psi_4\rangle \approx 0.45$ and $\langle\psi_6\rangle \approx 0.37$ for the respective ranks [A.5].

2.3 Phase transitions II: symmetry breaking

In many cases, phase transitions involve breaking the symmetry of the system [1, 26, 42]. In such instance, the high-temperature (low-concentration) phase usually possesses a higher symmetry than the low-temperature (high-concentration) one. If the phase transition does not require application of external fields, one refers to the symmetry change as spontaneous symmetry breaking (SSB).

In the context of LCs, the most important example is the Iso-N phase transition. In this case, the high-temperature phase is Iso. It has a full translational and orientational symmetry, which is called the Euclidean group $E(3)$

$$\text{Sym}_{\text{Iso}} = E(3) = \text{SO}(3) \times \mathbb{T}^3, \quad (2.14)$$

where $\text{SO}(3)$ is the group of all three-dimensional rotations and $\mathbb{T}^3$ are all translations.

On the other hand, the low-temperature phase is N. Firstly, the phase is invariant under rotations around the director (linear symmetry). Moreover, the director is actually a senseless vector – that is, $\hat{\mathbf{n}}$ and $-\hat{\mathbf{n}}$ are equivalent, thus the symmetry possessed the inversion center. Translational symmetry does not change. Consequently,

$$\text{Sym}_{\text{N}} = \text{D}_{\infty h} \times \mathbb{T}^3, \quad (2.15)$$

where $\text{D}_{\infty h}$ is the infinite dihedral group (the symmetry of a cylinder). The $\text{D}_{\infty h}$ is a subgroup of the $\text{SO}(3)$ group, which exemplifies the SSB in the context of the N-Iso phase transition.

An important aspect of the SSB arises due to ambiguity when choosing the symmetry-broken state. During the Iso-N phase transition, the system orders spontaneously and chooses the direction of $\hat{\mathbf{n}}$. When no additional constraints are imposed, it can be arbitrary, and the resulting states are energetically equivalent. This set of all possible symmetry-broken states is called the space of degeneracy. For the N phase, due to the senseless nature of $\hat{\mathbf{n}}$, it is the two-dimensional real projective space $\mathbb{RP}_2$. The space of degeneracy, together with the symmetry group, restores the $\text{SO}(3)$ symmetry of the system's Hamiltonian. The consequence of the energetical equivalence of SSB states is the presence of the so-called Goldstone mode. That is, the SSB state may diffuse freely within its space of degeneracy without any energetical penalty.

It is also instrumental to establish the connection between the SSB and the order parameters. The order parameters are a direct consequence of the SSB. When the symmetry is broken, an additional parameter is necessary to characterize the system. For the N phase, it is the nematic order parameter P_2 . In the Iso phase its value falls to zero, and thus it may be eliminated from the description.

The above considerations may be applied to other phase transitions, in particular, to the next N-SmA phase transition in the Iso-N-SmA phase sequence. There,

N is the high-temperature phase, and SmA is the low-temperature one. Symmetry breaking is on the level of $\mathbb{T}^3$ translational symmetry. In SmA, a full $\mathbb{T}^2$ symmetry is retained in two directions, while the continuous symmetry in the third direction becomes quantized with a period p : $\mathbb{T} \rightarrow \mathbb{T}(p)$. Consequently,

$$\text{Sym}_{\text{SmA}} = D_{\infty h} \times \mathbb{T}^2 \times \mathbb{T}(p). \quad (2.16)$$

Here, SSB introduces τ as an additional order parameter. The degeneracy space for the SmA phase is $\mathbb{RP}_2 \times U(1)$, where $U(1)$ is the space of degeneracy of the translational degrees of freedom (the phase of density modulation).

Lastly, it is important to discuss SSB in the N-N_F (uniaxial-ferroelectric) phase transition. There, the up-down symmetry of the N phase is broken: $D_{\infty h} \rightarrow C_{\infty v}$, where $C_{\infty v}$ is the infinite cyclic group (the symmetry of a cone). Again, the SSB requires introducing a new order parameter – in this case, the polarization M . The space of degeneracy of the orientational degrees of freedom is the two-dimensional sphere S_2 instead of $\mathbb{RP}_2$.

2.4 Phase transitions III: entropy

2.4.1 Entropic phase transitions

The third aspect of phase transitions that shall be discussed in the Thesis is the role of the system's entropy. In phenomenological thermodynamics, the free energy F of the system can be expressed in terms of the internal energy E , the temperature T , and the entropy S :

$$F = E - TS. \quad (2.17)$$

Under a constant temperature and confined to a constant volume, the stable state is the one that globally minimizes F . Minimizing F for a given T can be achieved by decreasing E or increasing S . Intuitively, entropy is described as a measure of disorder, i.e., the less ordered the system, the higher the entropy. A more precise definition is given by the microscopic Boltzmann formula

$$S = k_B \ln \Omega, \quad (2.18)$$

where k_B is the Boltzmann constant and Ω is the number of microstates corresponding to a given macrostate. In other words, the Boltzmann entropy measures the amount of *choice* one has. Usually, a disorder can be realized in more ways than an order², thus, the former is characterized by a larger entropy.

Consequently, during the phase transition from a less ordered state to a more ordered one, the entropy S is expected to decrease. In that case, the phase transition is allowed only when the internal energy E is lowered simultaneously so that the global minimum of F for a given T is achieved. The conclusion is mathematically accurate if we use Eq. (2.18) to define what is more or less ordered. On the other hand, order or lack thereof may also be understood intuitively. For example, a crystal is visually more ordered than its amorphous counterpart. If intuition

²For example, a vase can be shattered into pieces in many ways but be intact only in one way.

coincides with definition (2.18), one indeed observes a simultaneous drop in E , and such a phase transition is *energy driven*.

There are, however, systems where this is not the case. The simplest example are hard-core systems, where $E = E(T)$ is a function of the temperature only, thus it cannot be manipulated – the only way to decrease F is to increase S . Despite that, phase transitions that introduce order are also observed for such systems. The apparent contradiction shows that a naïve interpretation of the entropy fails in such a case. In reality, although increasing the order of one type of degree of freedom indeed partially increases the entropy, it alleviates the constraint imposed on other degrees of freedom by, for example, decreasing the excluded volume, which results in net entropic growth. Phase transitions based on this phenomenon are *entropy driven* [43]. The next section will illustrate the concept in question using the Onsager model of hard rods.

2.4.2 Onsager hard-rod model

After the discovery of uniform nematic phases, the LC community began the search for the molecular origin of the phase. One of the theories, due to Maier and Saupe [44, 45], assumed the interaction between the anisotropic polarizabilities of the molecules, which favored parallel alignment. At the same time, the model completely disregarded the molecular shape, which, as we now know, is a false assumption. However, Meier-Sauper-like models are still being developed and provide successful descriptions of some properties in many systems [46–50].

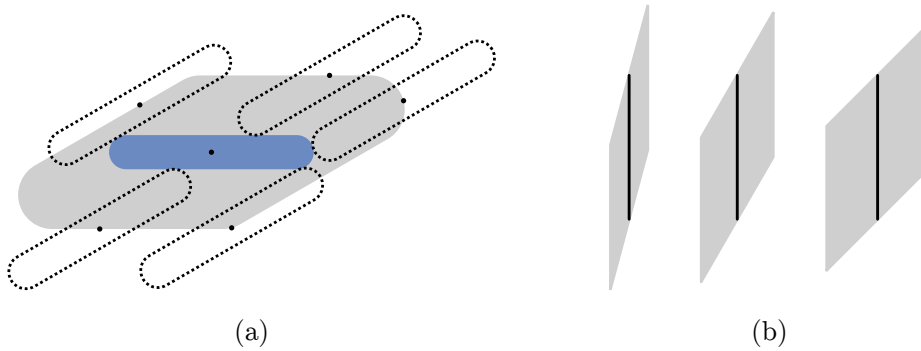


Figure 2.2: (a) An illustration of the excluded volume concept for a spherocylinder – the blue particle in the middle. The excluded volume is the gray area around it; all particles within it (illustrated by dotted contours) are guaranteed to intersect with the central spherocylinder. The shape of the excluded volume depends on the angle between the particles. (b) Excluded volumes (gray areas) for two infinitely thin rods (colored black) with an angle θ between them, from the left: $\theta = 15^\circ$, $\theta = 30^\circ$, and $\theta = 45^\circ$.

An arguably simpler model was proposed by Onsager [51]. The model does not assume any pair potential apart from the hard-core interaction between hard rods. Onsager showed that in the limit of infinitely thin rods the system must undergo the Iso-N phase transition. The phenomenon may be explained solely by invoking entropic arguments. In a high-temperature phase, both the positions

and orientations of the rods are disordered. Upon cooling, the excluded volumes [see Fig. 2.2(a)] of randomly oriented pairs of rods start to hinder their movement significantly. The excluded volume grows monotonically with the angle between the rods, and thus, it is the smallest when they are parallel [see Fig. 2.2(b)]. Consequently, although the parallel alignment decreases the orientational entropy, its translational counterpart increases by a significantly larger amount; thus, the nematic is spontaneously formed. The balance between different types of entropy is a common motif in the considerations of hard-core models and phase transitions in general.

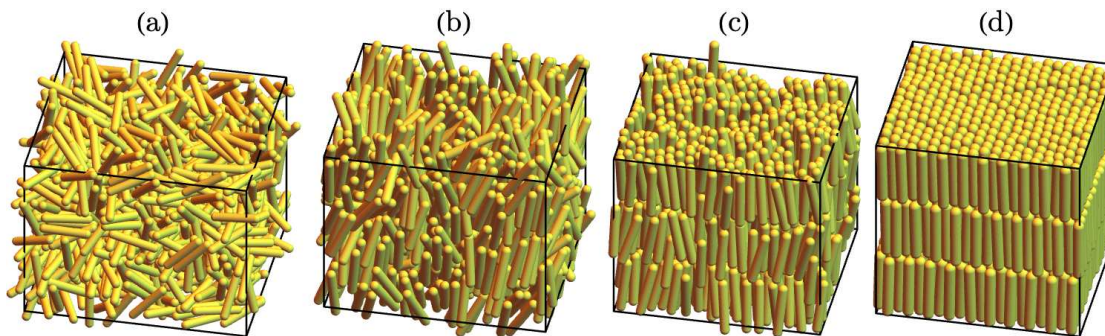


Figure 2.3: Snapshots of equilibrated systems of 900 hard-core spherocylinders simulated using RAMPACK Monte Carlo package (see Chap. 5). From the left: (a) isotropic liquid Iso, (b) uniaxial nematic N (c), type A smectic SmA, and (d) crystal Cr.

The Onsager-like model of hard spherocylinders, which are a finite counterpart of infinitely thin hard rods, was numerically simulated using the Monte Carlo method [28, 52]. Examples of snapshots recreated using the RAMPACK package are shown in Fig. 2.3. In addition to N, SmA and the crystalline structure were also observed, which contradicted the previous belief that the smectic phases require a specific type of molecular interaction. The N-SmA phase transition can also be explained through packing entropy. The presence of layers decreases the entropy of movement in the direction of the smectic wavevector $\mathbf{k}$, but, at the same time, provides a significant entropic gain from a less restricted movement in the directions orthogonal to $\mathbf{k}$. Similar arguments may be devised for the formation of the crystalline structure. There, an ordered structure facilitates the extended range of vibrational motion compared to a jammed, glassy counterpart.

2.5 Landau formalism

2.5.1 Landau theory

Landau's theory of phase transitions [53, 54] is a simple phenomenological model that provides a successful mathematical description of some aspects of phase transitions without resorting to the intrinsic properties of the system. Due to its generality, it appears outside the realm of thermodynamic systems, for example, in field theory, which is outside the scope of the Thesis. The Landau theory is based on the assumption that near the phase transition, the free energy is contin-

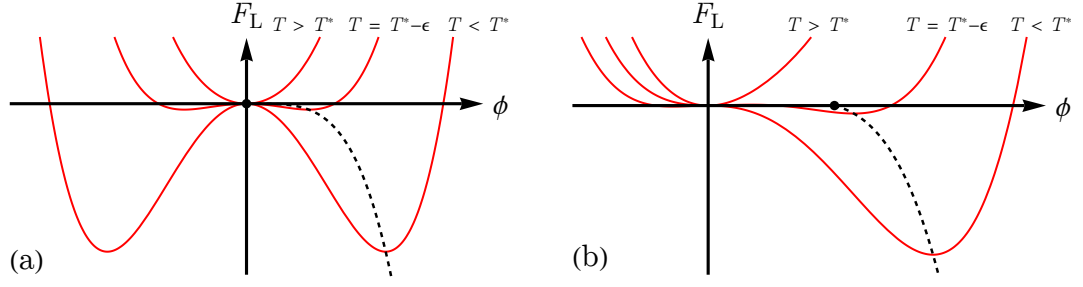


Figure 2.4: Landau free energy F_L (red lines) as a function of the order parameter ϕ for (a) the second order phase transition, and (b) the first order phase transitions. The free energy is drawn for three temperatures: above the critical temperature $T > T^*$, near the phase transition, but slightly below the critical temperature $T = T^* - \epsilon$, and further below the critical temperature $T < T^*$. The black dashed lines are the evolution of the global minimum of F_L for $T \leq T^*$, while the black point corresponds to $T = T^*$. Please notice the sudden jump of the minimizing ϕ value in panel (b) and the lack thereof in panel (a).

uous in the order parameter ϕ connected to the phase transition. Thus, one can apply a Fourier expansion. The simplest form of the Landau free energy is for the second-order phase transition

$$F_L(\phi) = F_0 + A(T - T_0)\phi^2 + B\phi^4, \quad (2.19)$$

where F_0 is the free energy at the transition, A and B are positive constants and $T_0 \equiv T^*$ is the critical temperature. In such a formulation, if $T > T_0$, the coefficient of the quadratic term is positive, and $\phi = 0$ minimizes F_L . However, if $T < T_0$, the coefficient becomes negative, and the minimizing solutions are given by

$$\phi^2 = \frac{A(T_0 - T)}{2B}. \quad (2.20)$$

Assuming the order parameter $\phi > 0$, we are left with one positive solution. Combining both regimes: $T > T_0$, $T < T_0$, we have

$$\phi = \begin{cases} 0 & \text{if } T \geq T_0, \\ \sqrt{\frac{A(T_0 - T)}{2B}} & \text{if } T < T_0. \end{cases} \quad (2.21)$$

The evolution of F_L with temperature is shown in Fig. 2.4(a). Notably, ϕ is a continuous function of T , reflecting the properties of the second-order phase transitions.

First-order phase transitions may be described in the Landau formalism by introducing a cubic term:

$$F_L(\phi) = F_0 + A(T - T_0)\phi^2 - C\phi^3 + B\phi^4, \quad (2.22)$$

where $C > 0$ is also assumed to be positive. The analysis of the equation shows that the global minimum is reached for

$$\phi = \begin{cases} 0 & \text{if } T > T^*, \\ \frac{3C}{8B} + \sqrt{\left(\frac{3C}{8B}\right)^2 + \frac{A(T_0 - T)}{2B}} & \text{if } T < T^*, \end{cases} \quad (2.23)$$

where $T^* = T_0 + C^2/4AB$ is the critical temperature. The evolution of F_L with temperature is shown in Fig. 2.4(b). The behavior at $T = T^*$ correctly reflects the nature of the first-order phase transition. Firstly, one observes a sudden jump $\phi = 0 \rightarrow C/2B$ in the order parameter when passing the critical temperature. Secondly, exactly at $T = T^*$ there are two equivalent global minima, which models the phase co-existence.

2.5.2 Landau-de Gennes formalism

One can apply the Landau free energy (2.22) to model the Iso-N phase transition by using the nematic order parameter $\phi \equiv P_2$. However, as signaled in Sec. 2.2.1, the $\mathbf{Q}$ -tensor better reflects the symmetry of the nematic phase. Thus, nematics are often described using the Landau-de Gennes free energy [1]

$$F_{\text{LdG}} = A(T - T_0)\mathbf{Q}^2 - C\mathbf{Q}^3 + B\mathbf{Q}^4. \quad (2.24)$$

The powers of $\mathbf{Q}$ denote rotationally invariant scalars obtained by summing the indices of $\mathbf{Q}$. It can be shown that the only independent terms are $\text{Tr } \mathbf{Q}^2$ and $\text{Tr } \mathbf{Q}^3$. The free energy is then written in an explicit form as

$$F_{\text{LdG}} = A(T - T_0) \text{Tr } \mathbf{Q}^2 - C \text{Tr } \mathbf{Q}^3 + B(\text{Tr } \mathbf{Q}^2)^2. \quad (2.25)$$

Landau-de Gennes formalism allows the incorporation of biaxiality³ into the theoretical description⁴. It is also possible to describe non-orthogonal axes using a nonsymmetric variant of the $\mathbf{Q}$ -tensor.

2.5.3 Oseen-Zocher-Frank free energy

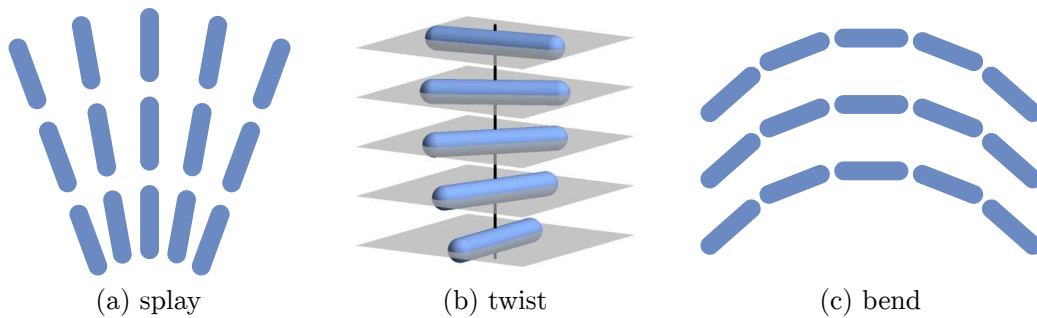


Figure 2.5: Illustration of the lowest order deformation modes: (a) splay, (b) twist, (c) bend. Splay and bend modes can be realized in two dimensions, while twist is essentially three-dimensional.

Until this point, all considerations were led with the assumption that the director field is uniform. This holds true only for non-modulated phases. However,

³Biaxiality means that the system is characterized not only by the director $\hat{\mathbf{n}}$, but also by a secondary axis orthogonal to $\hat{\mathbf{n}}$; an example is a system of cuboids where the particles align their sides with all three coordinate system axes.

⁴In that case, one must include higher powers of $\mathbf{Q}$ [36].

some of the nematic and smectic phases described in this thesis are not uniform. Thus, it is instrumental to provide a theoretical framework to describe the director field modulations. In the lowest order (quadratic in the $\mathbf{Q}$ -tensor), the deformations are usually treated in the form of Oseen-Zocher-Frank free energy [55–57] written using the director $\hat{\mathbf{n}}$

$$F_{\text{OZF}} = \int_V \frac{1}{2} K_{11} [\hat{\mathbf{n}}(\nabla \cdot \hat{\mathbf{n}})]^2 + \frac{1}{2} K_{22} [\hat{\mathbf{n}} \cdot (\nabla \times \hat{\mathbf{n}})]^2 + \frac{1}{2} K_{33} [\hat{\mathbf{n}} \times (\nabla \times \hat{\mathbf{n}})]^2 \quad (2.26)$$

$$= \int_V \frac{1}{2} K_{11} \mathbf{S}^2 + \frac{1}{2} K_{22} \mathcal{T}^2 + \frac{1}{2} K_{33} \mathbf{B}^2 \quad (2.27)$$

where K_{ii} , $i = 1, 2, 3$ are the Frank elastic constants weighting the deformation modes (splay, twist, and bend). $\mathbf{S}$, $\mathcal{T}$, and $\mathbf{B}$ are, respectively, the splay vector, the twist pseudoscalar, and the bend vector. The deformation modes are illustrated in Fig. 2.5.

In a uniform nematic, all elastic constants obey Ericksen inequalities $K_{ii} \geq 0$ [58]. As a consequence, any emerging modulations are energetically penalized. The situation changes when one allows one or more constants to become negative⁵. Then, the uniform nematic ceases to be the stable structure in favor of the modulated phases. It was argued that the shape effect alone can lead to softening or changing the sign of the elastic constants [59]. Consequently, a crescent shape of a particle is connected with a decrease of the K_{33} bend elastic constant, while a cone-like shape facilitates the softening of the K_{11} splay elastic constant.

One of the phenomena that can lead to unusually low values of elastic constants is the flexoelectric effect [59–62]. Flexoelectricity is the coupling of the transversal molecular polarization with the bend deformation or the longitudinal polarization with the splay deformation. Here, the mathematical treatment is exemplified for the bend deformation – the construction for the splay mode is analogous. First, it is assumed that the polar order $\mathbf{P}$ is encouraged in the system (for example, as mentioned above, by the molecular shape). It is done by incorporating the term $\mu(T - T_0)\mathbf{P}^2$ with $\mu > 0$. Flexoelectricity is described by the term $-\lambda \mathbf{B} \cdot \mathbf{P}$ ($\lambda > 0$). Ultimately, the free energy becomes

$$F = \int_V \frac{1}{2} K_{11} \mathbf{S}^2 + \frac{1}{2} K_{22} \mathcal{T}^2 + \frac{1}{2} K_{33} \mathbf{B}^2 - \lambda \mathbf{B} \cdot \mathbf{P} + \mu(T - T_0)\mathbf{P}^2. \quad (2.28)$$

Minimizing it w.r.t. $\mathbf{P}$ yields

$$F = \int_V \frac{1}{2} K_{11} \mathbf{S}^2 + \frac{1}{2} K_{22} \mathcal{T}^2 + \frac{1}{2} K_{33}^{\text{eff}} \mathbf{B}^2, \quad (2.29)$$

where

$$K_{33}^{\text{eff}} = K_{33} - \frac{\lambda^2}{\mu(T - T_0)}. \quad (2.30)$$

What follows is that K_{33}^{eff} becomes negative for $T < T_0 + \lambda^2/\mu K_{33}$.

⁵In such a situation, the addition of higher fourth-order stabilizing terms is needed.

Chapter 3

Phases with non-standard symmetry

As established in the last part of the previous Chapter, when one or more elastic constants K_{ii} , $i = 1, 2, 3$ become negative, a spontaneous director field modulation may arise in the system. Moreover, it is usually inherently coupled to some polarization order. This Chapter summarizes the key modulated and polar nematic and smectic phases. Several of these phases have been validated experimentally; some have been identified only in computational simulations, and others are purely theoretical. For historical accuracy, apart from phases connected with the fourth and fifth generations of nematics, cholesteric and blue phases are also briefly mentioned. All types of director and polarization field profiles (excluding the blue phases) important from the point of view of this work are gathered in Fig. 3.1.

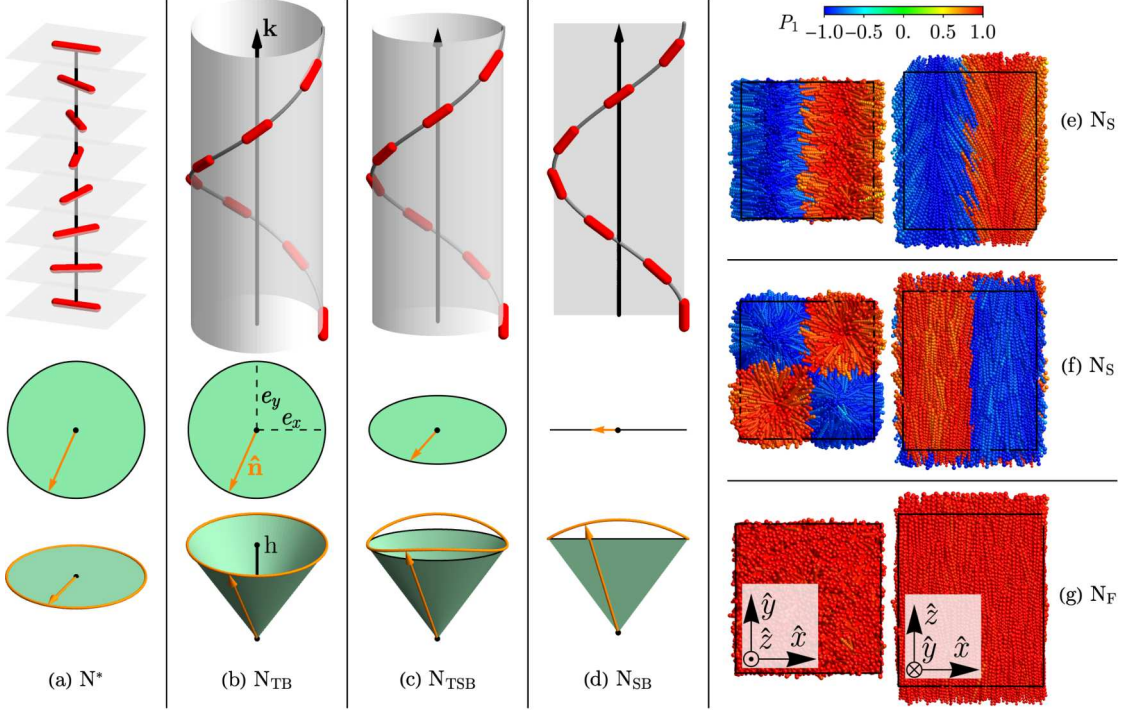
3.1 Historical phases – chiral systems

3.1.1 Cholesteric

The first LC phase observed by Reinitzer in 1888 for cholesteryl benzoate was a cholesteric N^* [10,63]. The structure is periodic (with the period p) in the direction of the wavevector $\mathbf{k} = (2\pi/p)\hat{\mathbf{k}}$, with $\hat{\mathbf{k}} = \mathbf{k}/\|\mathbf{k}\|$. If restricted to a single plane orthogonal to $\mathbf{k}$, the director $\hat{\mathbf{n}}$ is constant and lies within it; however, its direction changes when moving along $\mathbf{k}$. More precisely, the director field can be represented as

$$\hat{\mathbf{n}}_p(x, y, z) = \begin{pmatrix} \cos(2\pi z/p) \\ \sin(2\pi z/p) \\ 0 \end{pmatrix}. \quad (3.1)$$

Consequently, a helical structure is formed [see Fig. 3.1(a)]. The structure is chiral, that is, it has two variants with a different handedness. However, the mirror symmetry is not broken spontaneously in compounds that form N^* , because these molecules are inherently chiral. The modulation of the cholesteric is sometimes called single twist, which is a combination of twist and saddle-splay deformation modes – the latter is described in the next section.



3.1.2 Blue phases

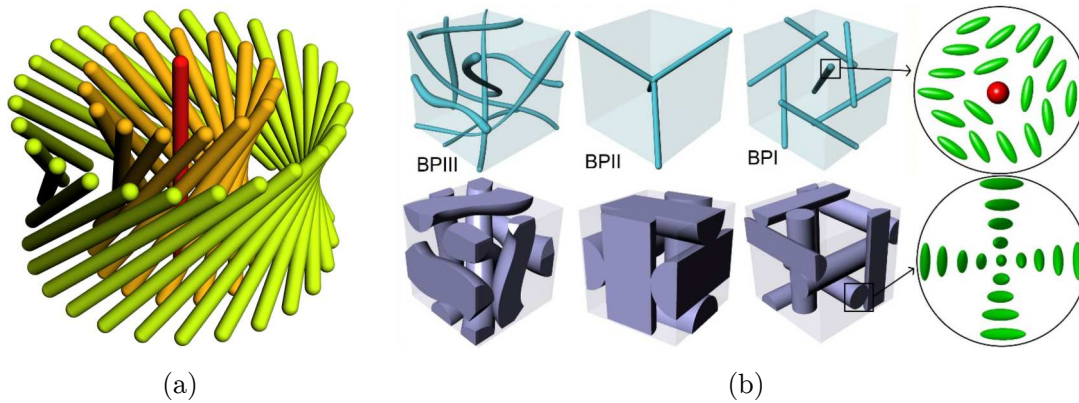


Figure 3.2: (a) Illustration of the double-twist director modulation in a cylindrical building block of the BPs. (b) Schematic representations of BPI, BP II, and BP III phases. The upper row shows the disclination lines, while the lower one shows the arrangement of cylinders. Please note that BPI and BP II phases form a periodic lattice, while BP III is disordered. The leftmost top panel illustrates how the particles (green spheroids) arrange near the disclination line (the red point), while the leftmost bottom panel shows how the particles follow the double-twist modulation within a cylinder. Reprinted from Ref. [64] with the permission of Multidisciplinary Digital Publishing Institute (MDPI).

For many compounds that form cholesteric, there are one or more LC phases between Iso and N^* , called blue phases (BPs) [11, 64–66]. The structure of BPs is rather complicated. Locally, the director field forms cylinders with the so-called double-twist (DT) modulation [see Fig. 3.2(a)]. In the middle of the cylinder, the director is parallel to its axis. However, when one moves away from it, the director leans in the transversal direction with an angle increasing with the distance. Consequently, DT modulation is rotationally symmetric, and when one restricts the analysis to a single plane containing the axis, the director follows a single twist modulation, as in N^* [see the rightmost bottom panel of Fig. 3.2(b)]. The DT cylinders are then arranged in periodic (BPI, BP II) or aperiodic (BP III) structures [see Fig. 3.2(b)]. The resulting global director field is not continuous; the DT cylinders are accompanied by linear defects between them, called disclinations. The distances between the cylinders and the disclination lines are on the order of several hundreds of nanometers. Consequently, one observes a Bragg reflection of the blue-light wavelength, hence the name.

An important aspect of BPs is their relationship to the Oseen-Zocher-Frank free energy. While Eq. (2.26) is how OZF energy is usually written, in reality, it contains an additional mode [65, 67]

$$F_{\text{OZF}}^* = F_{\text{OZF}} - \int_V \frac{1}{2} K_{24} \nabla \cdot [\hat{\mathbf{n}}(\nabla \cdot \hat{\mathbf{n}}) - (\nabla \cdot \hat{\mathbf{n}})\hat{\mathbf{n}}] \quad (3.2)$$

called the saddle-splay [68, 69] (see the illustrations therein), with K_{24} elastic constant playing a similar role as K_{ii} . The term is usually ignored, as it contains the

divergence $\nabla \cdot \dots$ and thus can be changed to the surface integral, which is negligible. However, in BPs, the surface integral is proportional to the system's volume, as it must also consider the disclination lines. Importantly, it can be shown that the saddle-splay term actually plays a role in stabilizing them [65].

Finally, the practical uses of BPs should be mentioned. Although for most compounds that stabilize the BPs, the temperature range of these phases is very narrow, on the order of several degrees [64, 70], there are compounds with a BP range as large as 50 °C, including the room temperature [71]. This allowed the creation of the blue phase mode LCD panel [72].

3.2 Bent-core systems

3.2.1 Twist-bend nematic

An important experimental discovery at the beginning of the 21st century was the observation of a novel nematic phase dubbed the twist-bend nematic N_{TB} for bent-core (banana-shaped) molecules [12–14] [see also Fig. 3.1(b)]. Similarly to N^* , the structure is chiral and possesses a period p ; however, the director, instead of being orthogonal to $\mathbf{k}$, forms a constant acute angle $\theta < \pi/2$ with it. Consequently, the director precesses around the cone as one moves along $\mathbf{k}$. Such a modulation is often called heliconical (helix + cone). Mathematically, the director field is described as

$$\hat{\mathbf{n}}_{p,\theta}(x, y, z) = \begin{pmatrix} \sin(\theta) \cos(2\pi z/p) \\ \sin(\theta) \sin(2\pi z/p) \\ \cos(\theta) \end{pmatrix}. \quad (3.3)$$

A defining feature of the N_{TB} phase is that the molecules for which it was observed are achiral. Thus, spontaneous mirror symmetry breaking (SMSB) occurs. Initially, SMSB was attributed to the so-called *conformational deracemization* [73]. Namely, because of internal flexibility, initially achiral molecules may exhibit chiral conformers, which eventually lead to the formation of heliconical domains. However, later, it was shown that N_{TB} also appears in purely repulsive systems of rigid, achiral bent-core shapes [24, 49] (see also [A.1-2]), disregarding the role of chiral conformers.

As discussed in Sec. 2.5.3, bend deformation is coupled to transversal molecular polarization. Indeed, the N_{TB} phase, both in the experiment and in simulations, is characterized by the polarization field, which is perpendicular to both the wavevector $\mathbf{k}$ and the director $\hat{\mathbf{n}}$:

$$\mathbf{M}_p = M \frac{\hat{\mathbf{n}} \times \mathbf{k}}{\|\hat{\mathbf{n}} \times \mathbf{k}\|} = \begin{pmatrix} M \sin(2\pi z/p) \\ -M \cos(2\pi z/p) \\ 0 \end{pmatrix}, \quad (3.4)$$

where M is the constant norm of the polarization vector.

The existence of SMSB in a system of achiral banana-shaped particles may be explained in terms of packing entropy and geometry. It is known that a bent-core shape of molecules softens the K_{33} bend elastic constant [59]. Bend deformation facilitates the sliding movement of particles, which provides an entropic gain.

However, a pure bend cannot fill the space uniformly without topological defects. Thus, it has to be accompanied by twist and/or splay deformation modes. In the case of the N_{TB} phase, twist introduces a smaller energetic penalty than splay and thus is chosen among the two.

Chiappini *et al.* [49] provided additional geometric arguments for the formation of N_{TB} . They noticed that the integral curves of the vector field given by (3.3) form helices with a constant curvature. By matching it with the curvature of the particle, they established the relation between the particle's arc radius R , period p , and conical angle θ

$$p = \pi R \sin(2\theta), \quad (3.5)$$

which was in line with the results of their simulations. Thus, the entropic arguments based on a facilitated sliding movement can be used to explain the preference of twist over splay.

3.2.2 Splay-bend nematic

When, instead of twist, splay deformation is incorporated, splay-bend nematic N_{SB} is formed [74, 75] [see also Fig. 3.1(d)]. The director field is described well by the equation

$$\hat{\mathbf{n}}_{p,\theta}(x, y, z) = \begin{pmatrix} \sin(\theta) \cos(2\pi z/p) \\ 0 \\ \sqrt{1 - \sin^2(\theta) \cos^2(2\pi z/p)} \end{pmatrix}. \quad (3.6)$$

The Oseen-Zocher theory predicts that N_{SB} should be more stable than N_{TB} if $K_{11} < 2K_{22}$ [75]. Nevertheless, there is little evidence of the existence of N_{SB} in thermotropic systems¹. However, it was reported in colloids [77]. Density functional theory calculations backed by computer simulations suggest that splay-bend modulation is coupled to density modulation and, instead of nematic, splay-bend smectic Sm_{SB} is formed [49] (see also [A.1-2]). This may align with the yet-unidentified smectic reported in [78].

Finally, it should be noted that the director field in all of N^* , N_{TB} , and N_{SB} (Sm_{SB}) phases may be merged into a single equation

$$\hat{\mathbf{n}}_{p,\theta_x,\theta_y}(x, y, z) = \begin{pmatrix} \sin(\theta_x) \cos(2\pi z/p) \\ \sin(\theta_y) \sin(2\pi z/p) \\ \sqrt{1 - \sin^2(\theta_x) \cos^2(2\pi z/p) - \sin^2(\theta_y) \sin^2(2\pi z/p)} \end{pmatrix}. \quad (3.7)$$

It describes the general biaxial structure of twist-splay-bend modulation, characterized by two θ_x , θ_y conical angles. In this formulation, N^* is described by $\theta_x = \theta_y = \pi/2$, N_{TB} is achieved by putting $0 < \theta_x = \theta_y < \pi/2$, while for N_{SB} $0 < \theta_x \leq \pi/2$ and $\theta_y = 0$. It is worth mentioning that the twist-splay-bend smectic Sm_{TSB} was observed in computer simulations as an intermediate state between N_{TB} and Sm_{SB} [49].

¹The formation of N_{SB} may, however, be forced using the electric field [76].

3.3 Conical systems

3.3.1 Ferroelectric nematic

In standard uniaxial nematics, only the directions of the molecular axes $\hat{\mathbf{a}}$ are ordered, while their senses remain random: the populations of “up” ($\hat{\mathbf{a}} \cdot \hat{\mathbf{n}} > 0$) and “down” ($\hat{\mathbf{a}} \cdot \hat{\mathbf{n}} < 0$) species are identical. Consequently, the system has an up-down symmetry. To describe it mathematically, one may consider the probability distribution of particle orientations. We assume the axial symmetry of both the particles themselves as well as the whole phase. Thus, the only independent variable is $\hat{\mathbf{a}} \cdot \hat{\mathbf{n}}$. Its distribution $f(\hat{\mathbf{a}} \cdot \hat{\mathbf{n}})$ may be expanded into Legendre polynomials

$$f(\hat{\mathbf{a}} \cdot \hat{\mathbf{n}}) = \sum_i \langle P_i \rangle P_i(\hat{\mathbf{a}} \cdot \hat{\mathbf{n}}), \quad (3.8)$$

with $\langle P_i \rangle$ – their expectation values (order parameters). The up-down symmetry is reflected by vanishing odd order parameters $\langle P_{2k+1} \rangle = 0$, $k = 0, 1, 2, \dots$. The situation changes in the ferroelectric nematic N_F , which is depicted in Fig. 3.1(g) for a system of taper-like particles. The up-down symmetry is broken, and the ordinary nematic order is accompanied by the polar order. Consequently, odd order parameters are no longer zero $\langle P_{2k+1} \rangle \neq 0$.

The idea that the nematic phase can be ferroelectric is more than 100 years old; it was first alleged in the paper of Born in 1916 [79]. Following the argumentation of Meyer [60], also featured in Sec. 2.5.3, one could expect the onset of longitudinal polar order in systems with softened K_{11} splay elastic constant, which is favored by molecular shapes with a broken up-down symmetry (cone-like). In fact, ferroelectric phases were found in lattice Monte Carlo simulations with asymmetric interactions at the two ends of the particle at the beginning of the 21st century [80]. Polar order was achieved even without introducing dipolar moments. Moreover, after adding them, ferroelectric nematic N_F was formed. In the experiment, it was finally discovered in 2017 for two compounds, called DIO [16] and RM734 [17, 18].

It is believed that two main molecular factors are necessary to stabilize the N_F phase – the conical shape and the presence of a dipolar moment [80, 81]. The first softens the splay elastic constant K_{11} , while the second stabilizes the polar order. One of the goals of the Thesis (more precisely, the articles [A.3-5]) was to assess the importance of the first factor.

3.3.2 Splay nematic

For the RM734 molecule, one observes a direct transition from N to N_F . On the other hand, for DIO, there is a third nematic between them: the splay nematic N_S [Fig. 3.1(e, f)]. Although the phase is globally apolar, it is built of locally polar domains with splay modulation. The presence of N_S is not unexpected – as noted earlier, the K_{11} splay elastic constant is lowered in conical systems, thus splay order may be promoted.

It is instructive to compare two competing local arrangements of two conical particles: antiparallel and parallel [see Fig. 3.3]. If antiparallel alignment is preferred, the polar order is not promoted. At the same time, adjacent particles do

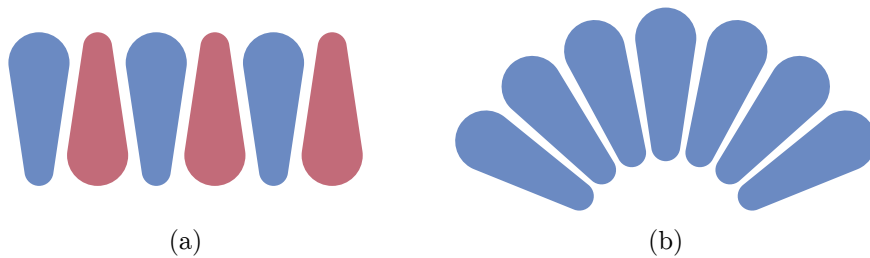


Figure 3.3: (a) Optimal packing of conical particles if local antiparallel alignment is preferred. The direction of molecular axes $\hat{\mathbf{a}}$ remains constant. (b) Optimal packing of conical particles if local parallel alignment is preferred. The molecular axes $\hat{\mathbf{a}}$ naturally splay.

not tend to splay [see Fig. 3.3(a)]. Consequently, an ordinary, uniaxial nematic N is formed. However, if parallel alignment is preferred, polar order must appear at least on the mesoscale (local domains) if not globally. At the same time, such an alignment promotes the splay deformation [see Fig. 3.3(b)]. In Sec. 3.2.1, when discussing the N_{TB} phase, it was argued that the bend deformation cannot fill the space uniformly. As the splay deformation is orthogonal to bend, it is subject to the same restrictions, which leads to the domain structure of N_S , with opposite polarizations and splay vectors in adjacent domains. If only splay deformation is allowed, the interface between the domains must be discontinuous, which results in topological defects. The more energetically favorable solution may be continuous with vanishing polarization and director fields at the interface; however, this results in a non-zero bend vector in this region.

Experimentally, it is known that N_S is locally polar, and periodic splay modulation is present. Although the exact mesostructure has not yet been established, it is generally alleged to be the so-called single-splay (SS) configuration [19, 82, 83]. Rosseto and Selinger, however, proposed alternative realizations of N_S : the double-splay (DS) [84].

In SS, the domains are infinite in two directions. The adjacent ones have opposite splay and polarization vectors. The example realization is shown in Fig. 3.1(e) (see also [85]). Ref. [84], in the first order, describes director and polarization fields of SS by

$$\hat{\mathbf{n}}(x) = \begin{pmatrix} \sin[\Theta(x)] \\ 0 \\ \cos[\Theta(x)] \end{pmatrix}, \quad \Theta(x) = \Theta_0 \sin(kx), \quad (3.9)$$

$$\mathbf{M}(x) = M \cos(kx) \hat{\mathbf{n}}(x), \quad (3.10)$$

where Θ_0 regulates the strength of splay modulation, $k = 2\pi/L$ is the wavevector, $L/2$ is the width of a single domain, and M is maximal local polarization modulus. The authors argued that those profiles work well close to the N - N_S critical point; however, sharper changes are observed away from it.

In the alternative variant, DS, the domains are infinite in one direction. They are stacked in a checkerboard pattern, where for each domain, all four neighbors

have opposite splay and polarization vectors [see Fig. 3.1(f)]. The first-order director and polarization fields are written as

$$\hat{\mathbf{n}}(x, y) = \mathcal{N}^{-1} \begin{pmatrix} \Theta_0 \sin(kx) \cos(ky) \\ \Theta_0 \cos(kx) \sin(ky) \\ 1 \end{pmatrix}, \quad (3.11)$$

$$\mathbf{M}(x, y) = 2M \cos(kx) \cos(ky) \hat{\mathbf{n}}(x). \quad (3.12)$$

with $\mathcal{N}^2(x, y) = \Theta_0^2 \sin(kx)^2 \cos(ky)^2 + \Theta_0^2 \cos(kx)^2 \sin(ky)^2 + 1$. Again, the equations better describe the fields closer to the critical point.

Rosseto and Selinger assessed the stability of both modulation types. DS was more stable for most temperatures in the region between the N-N_S and N_S-N_F critical points, with a narrow window of stability of SS near N, and only for a sufficiently small K_{33} bend elastic constant. This suggests that the DS variant is more likely to be realized in the experiment. It is important to note that the pure splay deformation is actually DS. In contrast, SS requires the incorporation of the second deformation mode, the saddle-splay (discussed in Sec. 3.1.2).

Chapter 4

Molecular Monte Carlo simulations

In statistical physics, few models are exactly solvable. The simplest example is the ideal gas law $pV = Nk_B T$. However it applies only to non-degenerate gases and, in particular, cannot be used to describe liquids. There are only a handful of more complicated, exactly solvable models, among which the most famous is the Ising model of spin systems in one [86] and two [87] dimensions. A broader class of settings, however, may be treated approximately. Some approaches are, for example, based on the virial expansion. For hard spheres, the virial coefficients can be computed exactly up to the fourth order [88], which allows one to describe a slightly degenerate gas. An even wider range of packing fractions η are covered by Padé approximations, such as the Carnahan-Starling equation [89]

$$Z = \frac{pV}{Nk_B T} = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3}, \quad (4.1)$$

and its generalizations to anisotropic shapes (e.g. Nezbeda equation [90]) or even mixtures of shapes (e.g. Boublik-Mansoori-Carnahan-Starling-Leland [91, 92]). Other important classes of models are based on a mean-field approach [79, 93, 94], allowing one to study various properties of systems and covering different regions of the phase diagram.

Nevertheless, approximate theories can provide only a limited insight into the system's properties and still need verification. Fortunately, many systems may be solved exactly by computer simulations. Computational results can then be cross-referenced with experimental data and, finally, used to verify theoretical models. This Chapter provides a summary of the Monte Carlo (MC) Metropolis-Hastings algorithm (MHA) [95, 96]. It is one of the first computational techniques developed for molecular research, predating Molecular Dynamics [97], which supports various types of systems within the same formalism. The Chapter is based mostly on the Allen, Tildesley [98], and Frenkel, Smit books [99], as well as Shell's lectures [100, 101].

4.1 Problem formulation

4.1.1 Statistical physics

All statistical properties of a thermodynamic system may be computed using an appropriate thermodynamic ensemble. If the system has a constant number of particles N , volume V , and is connected to a heat bath with constant temperature T , it is described by the canonical ensemble, where, for spherically symmetric particles, the probability of a microstate is given by

$$\rho(\mathbf{r}^N, \mathbf{p}^N) = \frac{1}{Q(N, V, T)} e^{-\beta \mathcal{H}(\mathbf{r}^N, \mathbf{p}^N)}. \quad (4.2)$$

Here, $\mathbf{r}^N$, $\mathbf{p}^N$ are, respectively, the positions and momenta of all N particles, $\beta = (k_B T)^{-1}$, $\mathcal{H}(\mathbf{r}^N, \mathbf{p}^N) = K(\mathbf{p}^N) + U(\mathbf{r}^N, \mathbf{p}^N)$ is the system's Hamiltonian (with K the kinetic part and U the interaction part). Finally, $Q(N, V, T)$ is the so-called canonical partition function

$$Q(N, V, T) = \frac{1}{h^{3N} N!} \int e^{-\beta \mathcal{H}(\mathbf{r}^N, \mathbf{p}^N)} d\mathbf{r}^N d\mathbf{p}^N, \quad (4.3)$$

where the factor before the integral comes from Maxwell-Boltzmann statistics. If the interactions $U(\mathbf{r}^N)$ do not depend on the momenta (which is usually the case), the integral over them can be done exactly, leading to

$$Q(N, V, T) = \frac{Z(N, V, T)}{\Lambda(T)^{3N} N!}, \quad (4.4)$$

where

$$Z(N, V, T) = \int e^{-\beta U(\mathbf{r}^N)} d\mathbf{r}^N \quad (4.5)$$

is called configurational integral, and $\Lambda(T) = (h^2/2\pi m k_B T)^{1/2}$ is the thermal de Broglie wavelength. The microstate distribution $\rho(\mathbf{r}^N, \mathbf{p}^N)$ separates into momentum and position degrees of freedom

$$\rho(\mathbf{r}^N, \mathbf{p}^N) = \rho(\mathbf{p}^N) \rho(\mathbf{r}^N) \quad (4.6)$$

with

$$\rho(\mathbf{p}^N) = \frac{e^{-\beta K(\mathbf{p}^N)}}{h^{3N} \Lambda(T)^{-3N}}, \quad (4.7)$$

$$\rho(\mathbf{r}^N) = \frac{e^{-\beta U(\mathbf{r}^N)}}{Z(N, V, T)}. \quad (4.8)$$

Both distributions are normalized: $\int \rho(\mathbf{p}^N) d\mathbf{p}^N = 1$ and $\int \rho(\mathbf{r}^N) d\mathbf{r}^N = 1$. The last nontrivial part is to calculate the configurational integral $Z(N, V, T)$.

The microstate distribution can eventually be used to compute the expectation values of thermodynamic observables, such as energy, pressure, or order parameters. For a quantity $A(\mathbf{r}^N)$ not depending on system momenta we have

$$\langle A \rangle = \int A(\mathbf{r}^N) \rho(\mathbf{r}^N) d\mathbf{r}^N = \frac{\int A(\mathbf{r}^N) e^{-\beta U(\mathbf{r}^N)} d\mathbf{r}^N}{\int e^{-\beta U(\mathbf{r}^N)} d\mathbf{r}^N}. \quad (4.9)$$

Integrals in both the denominator and the numerator are usually not possible to calculate analytically and are notoriously hard to compute via traditional numerical integration schemes.

4.1.2 Importance sampling

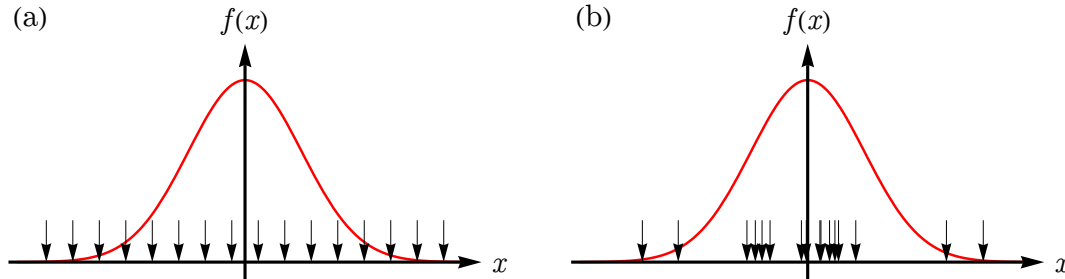


Figure 4.1: Illustration of the difference between (a) uniform sampling, and (b) importance sampling. In the first case, the samples of the integrand are taken uniformly, and many of them have a negligible contribution to the sum. On the other hand, when importance sampling is used, the samples are taken mostly from the range where the integrand is significant.

To formulate the basis for the MC algorithm, we start by exploring ways of computing definite integrals. As the simplest example, we take a one-dimensional integral

$$F = \int_{x_1}^{x_2} f(x) dx. \quad (4.10)$$

A basic method of computing it is the numerical quadrature, i.e., partitioning the range into discrete points and applying an appropriate weighted average to them. The easiest way is to take the points $t_1, t_2, \dots, t_n \in [x_1, x_2]$ with an equal distance $t_{i+1} - t_i = (x_2 - x_1)/(n - 1)$ and compute the sum

$$F = \frac{x_2 - x_1}{n} \sum_{i=1}^n f(t_i). \quad (4.11)$$

Other quadratures include the trapezoid and Simpson methods [102]. In principle, such approaches could be used to compute the integrals in (4.9); however, in practice, it is not feasible. If one samples only three points for each coordinate and takes rather few particles $N = 100$, it is still $3^{3N} = 3^{300} \approx 1.4 \times 10^{143}$ points in total, which is an exorbitant number even for the fastest supercomputers.

Another approach is a stochastic one. One takes a non-vanishing probability distribution $g(x)$ in the $[x_1, x_2]$ range and writes the integral as

$$F = \int_{x_1}^{x_2} \frac{f(x)}{g(x)} g(x) dx = \left\langle \frac{f}{g} \right\rangle_g \quad (4.12)$$

which evaluates to the expectation value of f/g under g distribution and can be estimated as a mean of a finite number n of samples X_i

$$F = \frac{1}{n} \sum_{i=1}^n \frac{f(X_i)}{g(X_i)}. \quad (4.13)$$

If one chooses $g(x)$ to be uniform $g(x) = 1/(x_2 - x_1)$, it yields

$$F = \frac{x_2 - x_1}{n} \sum_{i=1}^n f(X_i), \quad (4.14)$$

which is similar to (4.11), but the points are random instead of regular. This computation can already be called a Monte Carlo method, as random numbers are involved. Naturally, F estimated using Eq. (4.14) is subject to statistical fluctuations, thus a large enough number of samples n must be taken to obtain the desired precision.

Such a stochastic approach usually converges slower than the deterministic ones for low-dimensional integrals but is much better in higher dimensions, especially when the integral has a complex boundary. However, fundamental algorithmic complexity is still exponential in the number of dimensions (in our case, the number of particles). The situation changes if the distribution $g(x)$ is chosen carefully. That is, if $f(x)/g(x)$ is nearly constant, then significantly fewer samples are needed to achieve the convergence; optimally, $g(x) = f(x)$. This way of choosing x values is called importance sampling because the samples appear mainly in regions where $f(x)$ is significant, thus where the contribution to the integral is the largest. The concept is illustrated in Fig. 4.1.

For the expectation value of a thermodynamic quantity (4.9) a good choice is the microstate distribution $\rho(\mathbf{r}^N)$ itself, since for most real-world observables A the whole integrand $A(\mathbf{r}^N)\rho(\mathbf{r}^N)$ is significant only in regions where $\rho(\mathbf{r}^N)$ is large. The expectation value is then computed as

$$\langle A \rangle = \frac{1}{n} \sum_{i=1}^n A(\mathbf{X}_i^N), \quad (4.15)$$

where $\mathbf{X}_i^N$ are random variables sampled from $\rho(\mathbf{r}^N)$. At this point, it may seem that the complexity has not been lifted, because $\rho(\mathbf{r}^N)$ contains the configurational integral $Z(N, V, T)$. However, it is possible to sample points from the $\rho(\mathbf{r}^N)$ distribution without explicit knowledge of $Z(N, V, T)$. The next section is devoted to an appropriate method.

4.2 Metropolis-Hastings algorithm in NVT ensemble

There is a class of algorithms collectively named Markov chain Monte Carlo (MCMC), which can be used to sample random variables from a specific distribution. Markov chain is a statistical construct that can be imagined as a graph, where the vertices are states of the system and the directed edges represent the transitions between those states. Moreover, each edge is weighted with a probability of the transition to which it corresponds. Consequently, the weights of directed edges going out of a given vertex must sum up to 1. The Markov chain has a short memory – the current state depends only on the previous one, regardless of the past trajectory.

To provide a more precise mathematical description, we label the states using the index $m = 1, 2, \dots, K$, where K is their total number. We assume that at a given time, marked by i , the probability of state m is $\varrho_m(i)$. We denote the transition probability from state m to state n as π_{mn} . The proper normalization is imposed by demanding that

$$\sum_m \varrho_m(i) = 1 \quad \forall i \quad \text{and} \quad (4.16)$$

$$\sum_n \pi_{mn} = 1 \quad \forall m. \quad (4.17)$$

At each iteration, the probabilities of states evolve according to the equation

$$\varrho_m(i+1) = \varrho_m(i) - \sum_n \pi_{mn} \varrho_m(i) + \sum_n \pi_{nm} \varrho_n(i). \quad (4.18)$$

The first sum corresponds to the decrease in probability caused by transitions from the state m to other states, while the second sum is the increase in probability due to other states transitioning into the state m . When the number of iterations goes to infinity, the probabilities of states reach one of the stationary distributions, for which

$$\varrho_m(i+1) = \varrho_m(i) \equiv \varrho_m. \quad (4.19)$$

The stationary distribution has been denoted by dropping the time label i in $\varrho_m(i)$. Combining Eqs. (4.18) and (4.19) gives

$$\sum_n \pi_{mn} \varrho_m = \sum_n \pi_{nm} \varrho_n \quad \forall m. \quad (4.20)$$

The above relation is called the general balance condition.

In MCMC, the Markov chain is designed in such a way that its stationary distribution corresponds to the one from which the samples are supposed to be drawn. In other words, after performing a large enough number of iterations, the memory of the initial state is lost, and subsequent states of the Markov chain are properly distributed random variables of interest. One of the types of MCMC is the Metropolis-Hastings algorithm (MHA). Its design starts with the general balance condition (4.20). The construction is easier if an even stronger requirement is imposed:

$$\pi_{mn} \varrho_m = \pi_{nm} \varrho_n \quad \forall m, n. \quad (4.21)$$

This is called a detailed balance condition.

MHA divides a single Markov chain iteration into two steps:

1. Choosing a proposed change of state $m \rightarrow n$ with probability α_{mn} (move proposal probability).
2. Accepting the change with probability P_{mn}^{acc} (acceptance probability).

Consequently, the total transition probability is equal $\pi_{mn} = \alpha_{mn} P_{mn}^{\text{acc}}$. Combining it with the detailed balance condition (4.21) gives

$$\frac{P_{mn}^{\text{acc}}}{P_{nm}^{\text{acc}}} = \frac{\alpha_{nm} \varrho_n}{\alpha_{mn} \varrho_m}. \quad (4.22)$$

For convenience, one usually chooses a symmetric move proposal probability $\alpha_{mn} = \alpha_{nm}$. Then, Eq. 4.22 further reduces to

$$\frac{P_{mn}^{\text{acc}}}{P_{nm}^{\text{acc}}} = \frac{\varrho_n}{\varrho_m}. \quad (4.23)$$

The last step is to devise such P_{mn}^{acc} that Eq. (4.23) is true.

In the case of thermodynamic systems, the distribution is given by (4.8). Consequently, we require

$$\varrho_m = \frac{e^{-\beta U_m} d\mathbf{r}^N}{Z}. \quad (4.24)$$

Here, we have assumed that the states of the thermodynamic system are discrete, with potential energies U_m . Consequently, we must include the differential $d\mathbf{r}^N$ to convert the probability density $\rho(\mathbf{r}^N)$ into a dimensionless Markov chain state distribution ϱ_m . Discretization does not change the final formulas; moreover, it is in line with computer simulations, where the numerical precision is limited. Inserting (4.24) into (4.23) gives

$$\frac{P_{12}^{\text{acc}}}{P_{21}^{\text{acc}}} = \frac{Z^{-1} e^{-\beta U_2} d\mathbf{r}^N}{Z^{-1} e^{-\beta U_1} d\mathbf{r}^N} = e^{-\beta(U_2 - U_1)}. \quad (4.25)$$

For convenience of notation, we have put $m = 1$, $n = 2$. Importantly, the problematic configurational integral Z was eventually eliminated from the algorithm.

There is still a great deal of flexibility in choosing both the move proposal and acceptance probabilities. Move proposals are discussed in detail in Sec. 4.4. For P_{12}^{acc} , the most popular option satisfying the Eq. (4.25) is the Metropolis criterion

$$P_{12}^{\text{acc}} = \min \{1, e^{-\beta(U_2 - U_1)}\}. \quad (4.26)$$

There, each move that decreases the potential energy is accepted, while the ones that increase it are accepted with the probability $e^{-\beta(U_2 - U_1)}$. This choice facilitates reaching the equilibrium (stationary distribution) relatively fast.

It is important to note that the above considerations can be repeated for anisotropic particles with orientational degrees of freedom. The final formulas (in particular, the Metropolis criterion) remain identical in the latter case. The only difference is the necessity of perturbing both positions and orientations during move proposals.

4.3 Extension to NpT ensemble

Similarly to the NVT ensemble, one can construct the procedure for the NpT (isothermal-isobaric) ensemble. The NpT ensemble may be more convenient than the NVT ensemble when studying phase transitions, as it eliminates the problem of phase co-existence. It also facilitates creating dense (including crystalline) states – the system may be slowly compressed by gradually increasing the pressure. Last but not least, by independently relaxing the diagonal or even all matrix elements of the viscous stress tensor, one avoids creating frustration, which would appear

in the NVT ensemble. The corresponding ensemble is sometimes referred to as isothermal-isotension [103].

The algorithm is constructed by reiterating all the steps in the previous sections. We start from the configurational integral, which now gains the system's volume V as an additional degree of freedom

$$\Delta(N, p, T) = \int_0^\infty e^{-\beta p V} Z(N, V, T) dV. \quad (4.27)$$

Here, the momentum degrees of freedom are disregarded right from the beginning, as they were already discussed in Sec. 4.1.1. The probability density is given by

$$\rho(\mathbf{r}^N, V) = \frac{e^{-\beta U(\mathbf{r}^N) - \beta p V}}{\Delta(N, p, T)}. \quad (4.28)$$

Most of the further steps are identical, and we can already recite Eq. (4.23)

$$\frac{P_{12}^{\text{acc}}}{P_{21}^{\text{acc}}} = \frac{\varrho_2}{\varrho_1} = \frac{\rho(\mathbf{r}_2^N, V_2) d\mathbf{r}_2^N dV}{\rho(\mathbf{r}_1^N, V_1) d\mathbf{r}_1^N dV} = \frac{d\mathbf{r}_2^N}{d\mathbf{r}_1^N} e^{-\beta \Delta U - \beta p \Delta V}, \quad (4.29)$$

where $\Delta U = U_2 - U_1$ and $\Delta V = V_2 - V_1$. One must be careful when evaluating the differential ratio $d\mathbf{r}_2^N / d\mathbf{r}_1^N$. As the coordinates $\mathbf{r}$ are scaled together with V : $\mathbf{r}^N \propto V$, so are the differentials, thus $d\mathbf{r}_2^N / d\mathbf{r}_1^N = (V_2/V_1)^N$. More formally, $(V_2/V_1)^N$ is the Jacobian for the transformation of coordinates. Finally, we arrive at

$$\frac{P_{12}^{\text{acc}}}{P_{21}^{\text{acc}}} = \left(\frac{V_2}{V_1} \right)^N e^{-\beta \Delta U - \beta p \Delta V}. \quad (4.30)$$

Unsurprisingly, one usually uses the acceptance criterion similar to the Metropolis criterion, which in this case is sometimes called the Metropolis-Wood criterion:

$$P_{12}^{\text{acc}} = \min \left\{ 1, \left(\frac{V_2}{V_1} \right)^N e^{-\beta \Delta U - \beta p \Delta V} \right\}. \quad (4.31)$$

To improve numerical stability, it can be rewritten as

$$P_{12}^{\text{acc}} = \min \left\{ 1, e^{N \ln(V_2/V_1) - \beta \Delta U - \beta p \Delta V} \right\}. \quad (4.32)$$

It is important to note that the acceptance criterion has the same form regardless of the way the volume is changed. In particular, it stays the same for the most general moves in a triclinic (“floppy”) simulation box.

4.4 Performing moves

The last part of the MHA that was left unexplained earlier is the way of sampling the moves. For all types of trial moves (particle moves, volume moves) there are only two requirements: they have to be symmetric¹ and explore the whole phase

¹As noted earlier, this requirement is not essential, but it significantly simplifies the formulas for the acceptance probability.

space (ergodicity). This leaves much freedom in devising parameters that facilitate the fastest equilibration in a given case.

Most move types have free parameters that can control the extent of moves. If the average move extent is larger, accepted moves modify the system quicker; however, at the same time, the acceptance ratio (number of accepted moves divided by the total number of moves) lowers. Thus, an optimal size of the move should be chosen². In the past, the acceptance ratio of 50% was considered as a standard; however, later work showed that generally 20-25% is closer to the optimal choice [104, 105]. The tests performed using RAMPACK software (which is described in Chap. 5) confirm the latter recommendations.

The last part of this section summarizes the standard moves used in the NVT and NpT ensembles, as well as gives an example of a non-standard one, important for the simulation in the studies [A.3-5].

Translations

Translations can be sampled by simply drawing three random numbers from a uniform distribution $\mathcal{U}[-\Delta r, \Delta r]$ and constructing a displacement vector. The Δr parameter controls the extent of moves.

Rotations

Sampling the rotations is slightly more complicated. For axially symmetric particles, one may modify the two ends of the molecule's height using two independent displacements sampled in a way similar to the translation moves and normalize the height afterward. This approach was used, for example, in Ref. [106].

For general anisotropic molecules, a more elaborate scheme must be used. Fortunately, the rotations do not have to be distributed uniformly in the $SO(3)$ group, i.e., be controlled by the Haar measure [107], as long as the transition probabilities are symmetric. Consequently, one can first choose a random rotation axis, which is equivalent to selecting a point on a unit sphere, and then sample the rotation angle φ from a uniform distribution $\mathcal{U}[-\Delta\varphi, \Delta\varphi]$ with $\Delta\varphi$ controlling the move size³. There are many ways of sampling points on a sphere. The simplest is performed by repeatedly sampling a vector $\mathbf{w}$ from a uniform interval $[-1, 1]^3$ until $\|\mathbf{w}\| \leq 1$ and selecting the axis as $\mathbf{w}/\|\mathbf{w}\|$. This method has an optimized version [108], where a random point in a circle is transformed into a random point on a sphere.

Lastly, note that a translation and a rotation can be performed simultaneously in a single MC particle move. Tests on the RAMPACK software showed that rototranslation moves lead many systems to a faster thermalization than performing rotations and translation separately.

²Performance of moves can be measured as a mean square displacement versus the real CPU time (walltime).

³Please note that uniform sampling of rotation angles φ does not yield uniform distribution in the $SO(3)$ group, however it is symmetric and explores the phase space ergodically; thus, the scheme is eligible for MC sampling. To achieve a uniform distribution of rotations in the axis-angle representation, φ would have to be distributed with the probability density $\rho(\varphi) = (1/\pi)(\varphi - \sin \varphi)$.

Volume (box) moves

Before delving into how to sample the box moves, it is important to note how the positions $\mathbf{r}$ of particles change during them. We assume that the simulation box is spanned by three, not necessarily orthogonal, box vectors $\mathbf{v}_i$, $i = 1, 2, 3$. The absolute position $\mathbf{r}$ can be decomposed in $\mathbf{v}_i$ basis

$$\mathbf{r} = s_1 \mathbf{v}_1 + s_2 \mathbf{v}_2 + s_3 \mathbf{v}_3, \quad (4.33)$$

where $\mathbf{s} = [s_1, s_2, s_3]$, $s_i \in [0, 1)$ is the relative position. During the box move, the box vectors $\mathbf{v}_i$ change, while the relative positions of the particles $\mathbf{s}$ remain unaltered.

The way in which the simulation box is perturbed depends on how many degrees of freedom it has. For isotropic systems, it is sufficient to keep the shape of the box constant but change the overall scale. A scale change can be imposed by uniformly choosing a volume change from the $\mathcal{U}[-\Delta V, \Delta V]$ interval, with ΔV controlling the extent of moves. Near the phase transition, when the changes in volume tend to be significant, one may, instead of the uniform distribution, use the logarithmic distribution. Then, first, a number λ is chosen from the $\mathcal{U}[-\Delta \lambda, \Delta \lambda]$ interval, and the volume of the box is multiplied by a factor of e^λ .

To achieve anisotropic moves of an orthorhombic (cuboidal) box, each side of the box may be perturbed independently, using a linear or logarithmic distribution. The side lengths may be scaled all at once, or alternatively, one may alter only a single one, chosen at random.

Finally, in a general, triclinic (parallelepiped) box, the simplest way is to add small, random perturbations to $\mathbf{v}_i$. In a similar fashion to the side lengths of an orthorhombic box, the perturbations of box vectors may be applied to all of them at once, or to a single, randomly chosen one. The downside of such an approach is that, in addition to being sheared, the box is also rotated. To avoid it, one may correct the box's orientation after each perturbation so that $\mathbf{v}_1$ lies on the X axis, while $\mathbf{v}_2$ – in the XY plane. Alternatively, one may describe the box not by the box vectors but by three scale and three shear factors and operate on them.

Flip moves

The flexibility of the MHA allows one to introduce an arbitrary move type to facilitate faster equilibration. As an example, one can refer to the articles [A.3-5] regarding conical systems. In higher densities, nematic-like order is present, and adjacent, tightly packed particles are either parallel or antiparallel. To flip its polarization, a particle must rotate by 180° degrees, which requires passing a high free-energy barrier. Consequently, it is a rare event if only standard rotations with small extents are applied. However, full relaxation of the polarization axes is needed to achieve the true equilibrium. Thus, we introduced additional moves in which the particle axes are flipped in a single step. Such moves can be performed more rarely than translations and rotations, for example, every tenth time.

4.5 Additional remarks

Before closing this Chapter with a complete example of how MHA can be implemented in a real-world scenario, several additional comments are due.

Periodic boundary conditions

The system is confined to a simulation box with a finite volume. On the other hand, while performing translations, the particles may escape its bounds. Rejecting such moves would break the detailed balance conditions. A solution would be to introduce hard or soft walls. However, the presence of an interface may have an unwanted effect on the system properties. Thus, one usually resorts to using the periodic boundary conditions (PBC). Then, when a particle passes the bounds of one of the box walls, it reappears near the opposite one. Generally, in a triclinic box, PBC can be realized by converting the absolute position $\mathbf{r}$ of a particle to the relative one $\mathbf{s}$ and adding such integer numbers to each of the components, that the correct range is restored:

$$\mathbf{s} \rightarrow \mathbf{s} + [k, l, m] \in [0, 1)^3, \quad k, l, m \in \mathbb{Z}. \quad (4.34)$$

Two simulation phases

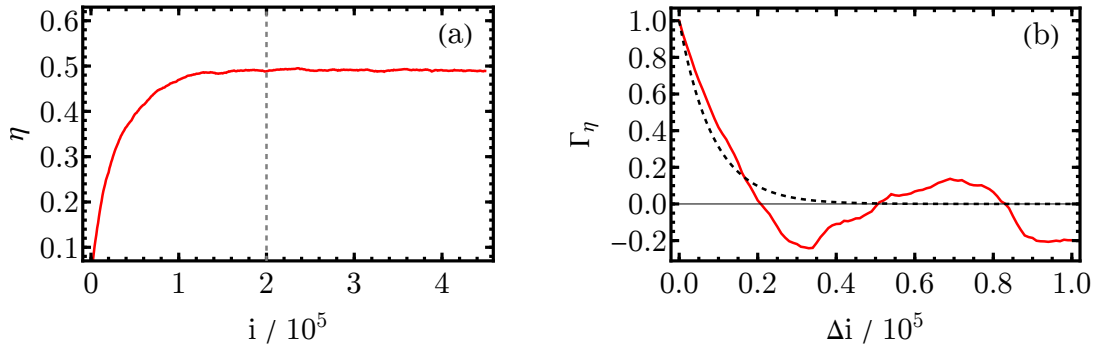


Figure 4.2: (a) The dependence of packing fraction η on the cycle number i (red line) for a hard-sphere liquid, compressed from a slightly degenerate gas. The gray dashed line separates the equilibration and production phases. (b) Autocorrelation function Γ_η (red line), Eq. (4.35) of the same system as a function of cycle number difference Δi , calculated in the production phase ($i > 2 \times 10^5$). The black, dashed line is an exponential fit $\Gamma_\eta(\Delta i) = e^{\Delta i/i_\Gamma}$, with $i_\Gamma \approx 8600$. Please note that the numerical values of Γ_η may be negative, as they are prone to statistical fluctuations (decreasing with the length of the production run).

Monte Carlo simulation starts with an initial configuration, which usually is an artificial low-probability⁴ state of the Boltzmann distribution, for example, a diluted crystal. Thus, including it in the averages would introduce a significant bias. Consequently, simulations are usually divided into two stages: the equilibration run and the production run. During the equilibration stage, the system loses

⁴Here, low-probability means practically zero, with the first passage time (starting from a high-probability state) possibly exceeding the age of the universe.

memory of the initial states. Then, in the production run, the averages are gathered. The length of both phases varies greatly, from several hundreds to hundreds of millions of full MC steps⁵. An example equilibration curve for a hard-sphere liquid is shown in Fig. 4.2(a). Please note the plateau after $i > 2 \times 10^5$ iterations. The expectation value of the packing fraction η may be computed in this region.

Including rejected moves

In MHA, transitions are realized via a two-step process: move proposal (with probability α_{mn}) and move acceptance (with probability P_{mn}^{acc}), where the net transition probability is $\pi_{mn} = \alpha_{mn} P_{mn}^{\text{acc}}$. Importantly, a rejected move proposal is also a valid step in the Markov chain. Consequently, all moves, whether they modify the system or not, must be included in the averages. Failing to do so would effectively result in sampling the states from a distribution different from (4.8) or (4.28).

Estimating the error of the mean

Assuming a sufficiently long equilibration time, the subsequent states produced by the MHA have a correct distribution. However, the samples are not uncorrelated because a single Monte Carlo step modifies the system only slightly. Although the mean $\langle A \rangle$ and variance $\sigma^2(A)$ of the distribution of observable A can be computed using the standard formulas despite the correlations, one must be careful when computing the error of the mean $\sigma^2(\langle A \rangle)$. The factor that the correlations contribute to $\sigma^2(\langle A \rangle)$ can be expressed using the autocorrelation function Γ_A , defined as [109]

$$\Gamma_A(\Delta i) = \lim_{i \rightarrow \infty} \frac{\langle [A(i) - \langle A \rangle][A(i + \Delta i) - \langle A \rangle] \rangle}{\sigma^2(A)}, \quad (4.35)$$

where $A(i)$ is the instantaneous value of A at a step i . Then, $\sigma^2(\langle A \rangle)$ can be computed as

$$\sigma^2(\langle A \rangle) = \frac{\sigma^2(A)}{n/(2n_\Gamma + 1)}, \quad (4.36)$$

where n is the total number of samples and

$$n_\Gamma = \sum_{\Delta i=1}^{\infty} \Gamma_A(\Delta i). \quad (4.37)$$

Analysis of Markov chains shows that the correlation decay is asymptotically exponential $\Gamma_A(\Delta i) \approx e^{-\Delta i/i_\Gamma}$. Thus, we can estimate

$$n_\Gamma \approx \frac{1}{e^{1/i_\Gamma} - 1}. \quad (4.38)$$

The correlation time i_Γ can be calculated by fitting the exponential function to the numerical values of $\Gamma_A(\Delta i)$ [see Fig. 4.2(b)]. Assuming $i_\Gamma \gg 1$, we have $\sigma^2(\langle A \rangle) \approx (2i_\Gamma/n)\sigma^2(A)$, thus a good estimation of $\sigma^2(\langle A \rangle)$ is also given by taking samples every $2i_\Gamma$ MC steps and calculating the variance in a standard way. It is also important to mention the so-called block average method, which does not require fitting the exponents. The interested reader is referred to Refs. [99, 110].

⁵A step is understood as a single volume move and perturbing each particle on average once.

4.6 Complete algorithm

To finalize this Chapter, the information featured in previous sections will be reiterated in a practical example of how MHA in the NpT ensemble can be used in a general system of anisotropic particles. Namely, we assume that the particles are not axially symmetric, and thus, full rotations must be used. We also assume that an anisotropic relaxation of an orthorhombic box is needed to prevent frustration in the system. Consequently, the box is described by three side lengths: a_1 , a_2 , and a_3 . The complete algorithm may be summarized as follows.

1. Prepare the initial configuration. It may be a slightly diluted crystalline lattice of some type or a final snapshot of the same system under different pressure.
2. Perform a full MC step for the equilibration phase:
 - (a) Perform a particle move:
 - i. Pick a random particle i .
 - ii. Translate the particle i by a random vector: $\mathbf{r}_i \rightarrow \mathbf{r}_i + \Delta\mathbf{r}_i$, $\Delta\mathbf{r}_i = [x_1, x_2, x_3]$, with x_i drawn from a uniform distribution $\mathcal{U}[-\Delta x, \Delta x]$. If necessary, correct the position according to PBC.
 - iii. Rotate the particle i by a small, random rotation, constructed from a random axis $\hat{\mathbf{a}}$ and random angle φ . Random axis $\hat{\mathbf{a}}$ can be chosen by sampling points $\mathbf{x}$ uniformly in a cube until $\mathbf{x} \leq 1$. Then $\hat{\mathbf{a}} = \mathbf{x}/\|\mathbf{x}\|$. Random angle φ is chosen from a uniform distribution $\mathcal{U}[-\Delta\varphi, \Delta\varphi]$.
 - iv. Test if the move should be accepted. To do so, calculate the change of the potential energy $\Delta U = U_2 - U_1$ caused by the move. If $\Delta U \leq 0$, accept the move. Otherwise, if $\Delta U > 0$, draw a number t from a uniform distribution $\mathcal{U}[0, 1]$ and accept the move if $t \leq e^{-\beta\Delta U}$.
 - (b) Repeat step (a) N times.
 - (c) Perform a volume move:
 - i. Pick a random box side a_i ($i = 1, 2, 3$).
 - ii. Sample λ from a uniform distribution $\mathcal{U}[-\Delta\lambda, \Delta\lambda]$. Scale the side length by $a_i \rightarrow e^\lambda a_i$ and all positions accordingly.
 - iii. Test if the move should be accepted. To do so, compute $\Delta G = N \ln(V_2/V_1) - \beta\Delta U - \beta p\Delta V$, where $\Delta U = U_2 - U_1$ and $\Delta V = V_2 - V_1$, are changes of, respectively, potential energy and box volume. If $\Delta G \geq 0$, accept the move. Otherwise, if $\Delta G < 0$, draw a number t from a uniform distribution $\mathcal{U}[0, 1]$ and accept the move if $t \leq e^{\Delta G}$.
 - (d) While performing particle and volume moves, keep track of how many moves were accepted.

3. Repeat step 2. until the system is equilibrated. It may take up to several hundred million cycles. Every n cycles (for example, $n = 100$), evaluate the current acceptance ratios. If the target acceptance ratios (around 20%) are not met, increase or decrease the corresponding Δx , $\Delta\varphi$, $\Delta\lambda$ step sizes. The adjustments may be stopped after the desired ratios are reached.
4. After equilibration, start the production run, where the averages are gathered. Repeat step 2. as many times as needed to obtain adequate statistical errors of the observables. It is wasteful to compute observables after each MC step – doing it every $10^3 - 10^5$ steps, depending on the system, should suffice. Do not adjust the step sizes in this stage – it may spoil the detailed balance condition.

The details of particular steps (i.e. the way of sampling moves) may be adjusted to a given scenario. Before launching large-scale simulations, it is a good practice to optimize the simulation parameters by performing tests on a smaller scale.

Chapter 5

RAMPACK simulation package



Figure 5.1: The logo of RAMPACK (Random And Maximal PACKing PACKage).

The previous Chapter discussed how Metropolis Monte Carlo method (more precisely, Metropolis-Hastings algorithm) can be used to computationally study thermodynamic systems. The MC method is relatively simple while, at the same time, it retains flexibility. Consequently, the code is highly reusable between different scientific projects. However, although the main algorithm is rather straightforward, extensive optimizations must be implemented to simulate thousands of particles for hundreds of millions of full MC cycles within a reasonable timeframe (up to a couple of weeks).

To provide a solid software basis for the computational work done for the articles [A.1-5] (and more in the making), an original open source simulation package, RAMPACK, was prepared and is continuously improved. Its name stands for **R**andom **A**nd **M**aximal **P**ACKing **P**ACKage. Ultimately, it is intended to provide a consistent framework for various types of MC-like methods, extending beyond typical equilibrium systems, for example, the Torquato-Jiao scheme [111] for maximally random jammed (MRJ) states [112]. The source code, together with user documentation and the whole history of releases, is hosted on GitHub:

→ <https://github.com/PKua007/rampack>

The software is versioned semantically (see Sec. 5.2.3), and as of the time of writing the Thesis, the newest stable release is v1.2.0.

Similar general-purpose molecular simulators include LAMMPS (MD) [113], and HOOMD-blue (MD, MC) [114]. Preparing one's own simulation software has several advantages. One of them is full control of what is possible to simulate. For example, some specific shape classes, such as a convex hull of two spheres

with different radii, that are used in modeling a molecule with a broken up-down symmetry are unavailable in existing toolkits. Secondly, it is possible to optimize performance for specific use cases. RAMPACK, while remaining general, is tailored specifically for highly elongated shapes needed to study the LC phases.

5.1 Architecture

5.1.1 Design philosophy

Before delving into the details of RAMPACK's architecture, its general design philosophy will be presented. Setting design goals from the beginning of software development is a vital step that facilitates the whole process and allows one to avoid rewriting large parts of the codebase in the future. For the RAMPACK toolkit, the following assumptions were put forward:

1. Simulations must be efficient and optimized. Simulating LC phases of elongated molecules requires the accommodation of at least four molecular lengths in a simulation box, which translates to several thousands of particles. Moreover, relaxation may be slow, requiring tens or even hundreds of millions of MC cycles.
2. Apart from single-thread optimizations, a parallelization scheme must be used, eventually incorporating GPGPU (general-purpose graphics processing unit) computing and scaling up beyond a single node in a computing cluster. Thus, it must be possible to include NVidia/AMD kernel code and use multi-node communication protocols, such as MPI (Message Passing Interface).
3. The software has to be general and extensible. The work needed to introduce additional shapes, interactions, types of moves, observables, etc., must be minimized, with a low risk of breaking the existing code. This may be achieved by using an object-oriented language and employing object polymorphism.
4. An array of different output formats should be available. It is needed for further analysis and visualization of simulation results. The formats must be recognizable by third-party software, such as Wolfram Mathematica [115] or Ovito [116].
5. The package, apart from the simulation code, should contain basic analysis tools. This includes the computation of observables, such as the packing fraction or order parameters, as well as basic histograms and correlation functions. It should be possible to do the analysis on-the-fly, during a simulation, as well as afterwards. The second part is especially important, as it may not be fully known *a priori* what should be computed. Consequently, simulation trajectories must be recorded in a compact, binary format.
6. The software has to be user-friendly, with a convenient way of defining the course of a simulation. Moreover, descriptive error messages can significantly reduce the time needed to fix wrong configurations, as well as locate software bugs.

7. In computational science, it is a common practice to keep a separate code for each research project, together with the data. Such an approach is prone to errors, and to correct them, many copies of the codebase must be altered. Thus, it should be possible to simulate different types of systems without rewriting and recompiling the software, apart from the time when new features are added.
8. The software should be backward compatible. It means that a newer release should be able to read older input files and outputs. This facilitates revisiting previous results after some time. A good framework for backward compatibility is semantic versioning.

To achieve the goals, C++ was chosen as a programming language. It is object-oriented and features class inheritance and object polymorphism, facilitating creation of necessary abstractions. At the same time, incorporating GPU kernel code and MPI communication subroutines is possible without additional compatibility layers. A fairly recent C++17 version was used. It includes quality-of-life features, such as lambda expressions, smart pointers, `std::optional`, `std::variant`, or `std::any`, and is commonly supported on computing clusters.

Currently, RAMPACK is distributed as a command-line tool with tab completion, together with the source code. The configuration is performed through input files and using the command-line arguments (see Sec. 5.3). In the future, it will also be shipped as a static-linked C++ library, together with Python bindings. The software can utilize all cores on a single computing node. Ultimately, it is planned to scale beyond a single node (using MPI) and incorporate GPGPU.

5.1.2 Simulation pipeline

Simulation box

The basic component of the simulation is a simulation box filled with the particles. A particle is understood as a single rigid body. The absolute positions¹ of particles are stored as three double-precision floating-point coordinates in a single, flat array, facilitating coalesced access with an improved memory bandwidth and more frequent cache hits. Orientations are stored as double-precision three-dimensional matrices, also in a continuous memory space. They were chosen over the quaternions because matrix-vector multiplication requires less floating-point operation than a rotation of a vector by a quaternion. Moreover, in the most recent, yet-unreleased version, there is a third raw byte array accommodating auxiliary particle data (shape parameters) for polydisperse systems.

The triclinic simulation box is represented by a matrix $\mathbf{V}$, where the columns are the subsequent box vectors $\mathbf{v}_j$. Namely, $V_{ij} = v_j^{(i)}$, with $v_j^{(i)}$ – i th coordinate of the j th box vector. Such a representation gives a simple mapping between absolute

¹Absolute positions were chosen over relative positions due to less computations needed for particle moves, which usually consume most of the walltime.

$\mathbf{r}$ and relative $\mathbf{s}$ coordinates:

$$\mathbf{r} = \mathbf{V}\mathbf{s}, \quad \text{and} \quad (5.1)$$

$$\mathbf{s} = \mathbf{V}^{-1}\mathbf{r}. \quad (5.2)$$

Both $\mathbf{V}$ and $\mathbf{V}^{-1}$ matrices are stored in memory. The box is allowed to rotate when the triclinic box moves are applied. As the particles do not rotate together with the box, it facilitates collective perturbations of orientations.

By default, the box has periodic boundary conditions in all directions. One may also toggle hard walls for each direction separately.

Runs

The whole simulation scheme consists of one or more runs. For the first run, the initial configuration of particles is either generated procedurally based on the specification or loaded from an external file. Then, each final snapshot of a previous run becomes the initial snapshot for the next one.

There are two types of runs:

1. **Integration** A standard MC sampling in the NVT or NpT ensemble. It is divided into two phases: *thermalization* (equilibration) phase and *averaging* (production) phase. In the thermalization phase, move extents are adjusted to achieve the acceptance ratio around 20%. The adjustment is turned off in the averaging phase.
2. **Overlap relaxation** A specialized MC scheme for hard-core shapes targeted for eliminating overlaps. To achieve this, all moves decreasing the number of overlaps are always accepted, and the ones increasing this number are always rejected, while if the number stays the same, perturbations are accepted according to the standard Metropolis criterion². The overlap relaxation run does not have the averaging phase.

Each run has a set of parameters that constitute the *simulation environment*. These include temperature, pressure, as well as types of particle and box moves. If not changed explicitly, the environment is inherited from the previous run.

Particle move types may be arbitrarily combined. The following ones are available: translation, rotation, rototranslation, and flip (180-degree rotation of the long molecular axis). The simulation box may be perturbed in a variety of ways, including linear or logarithmic isotropic and anisotropic scaling, as well as general triclinic deformations. Scaling may be turned off for an arbitrary combination of directions, which is useful for simulations with walls³.

²Such a procedure can be justified by considering a soft core potential, where two overlapping particles have constant energy U , while the disjoint ones do not interact. The overlap relaxation scheme is a limiting case with $U \rightarrow \infty$.

³Simulations with moving (“piston”) walls are also possible.

Data analysis

RAMPACK packages MC integration together with basic data analysis tools. It is done by defining two types of observables:

1. **Normal observables** Observables with up to several components, for example, a value of smectic order parameter τ and its Miller indices hkl . A limited number of the subvalues means that they can be juxtaposed in a single row of a table. The components can be *interval*, for which the average can be calculated, or *nominal*, for which it is not possible. In the previous example, τ is an interval component, while hkl are nominal. Normal observables can be computed in both the thermalization and averaging phases. Among others, the following normal observables are available in the toolkit: number density $\rho = N/V$, packing fraction η , compressibility factor $Z = pV/Nk_B T$, nematic order P_2 , smectic order τ , and bond order ψ_α .
2. **Bulk observables** Observables with a large number of subvalues, such as whole plots or histograms, meant to be stored in separate files. They are ensemble-averaged in an already equilibrated system; thus, they are gathered only in the averaging phase. Examples of bulk observables include: density histograms (in one, two, or three dimensions), binned functions (such as the dependence of components of molecular axes on the position in the box), or correlation functions (computed in linear, polar, or radial coordinates).

Both types of observables may either be collected on-the-fly (during the simulation), or afterward, using a recorded trajectory.

Output types

RAMPACK produces five main types of outputs:

1. **Final snapshot** A single, fixed simulation frame, captured at the end of a run. It includes the shape of the box, as well as the positions and orientation of the particles. The native format is called RAMSNAP. It is a human-readable text file with all the above information plus metadata (such as the number of cycles or move extents). It can be used to resume an interrupted run. Other snapshot formats are Wolfram, recognized by Wolfram Mathematica, and XYZ, recognized, for example, by Ovito.
2. **Trajectory** A collection of simulation frames in a single run, recorded every n cycles. They capture the changes of the simulation box and the particles within. The internal representation is called RAMTRJ. It is a compact, binary format, where positions and orientations are stored using a minimal number – six – of double-precision floating-point values (three position coordinates and three Tait-Bryan angles [117]). Moreover, the multi-frame XYZ format, recognized, for example, by Ovito, is also available.
3. **Observable snapshots** A single, CSV-like tabular file, where each row stores instantaneous values of normal observables, computed every n cycles in a single run. The observables are gathered in both the thermalization and averaging phases.

4. **Observable averages** Averages of the interval values of normal observables, computed in the averaging phases, and outputted as a single row. The results for multiple runs can be appended to a single file, which can be directly used to plot their dependence on system parameters (temperature, pressure).
5. **Bulk observables** For each run, ensemble-averaged bulk observables can be outputted to their own separate files.

There are also other helper output types, such as a 3D model of the particle's shape (in Wolfram or Wavefront OBJ [118] format), or the preview of the initial system configuration.

5.1.3 Acceleration structures

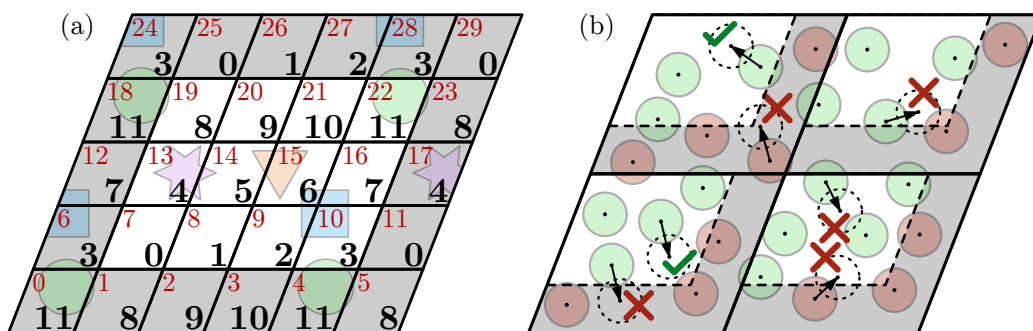


Figure 5.2: (a) Illustration of an efficient implementation of CLLs in two dimensions. The white grid cells are real cells, while the gray grid cells are ghost cells. Repeated shapes with the same color represent a real particle and its mirror reflections in the ghost cells. The larger, black, bold numbers in the lower right corner of each cell are the flat indices of the cell heads array, while the smaller, brown numbers in the upper left corner represent the flat indices of the cell mapping array. Please note that finding, for example, the lower left neighbor of a real cell can always be achieved by subtracting seven from the corresponding index in the cell mapping array. (b) Illustration of the domain division technique in two dimensions. Here, four domains are used (separated by black solid lines). The white areas represent active regions (with green particles), while the gray areas represent ghost layers (with red particles). The particles in ghost layers are stationary. For particles in the active regions, all moves placing them inside the ghost layers are rejected, while the remaining ones are accepted according to the standard Metropolis criterion.

In a naïve implementation of the MC integration scheme, a single MC step has a $\mathcal{O}(N^2)$ time complexity in the number of particles N . The complexity can be reduced to $\mathcal{O}(N)$ when appropriate acceleration structures are applied. The commonly used ones are Verlet lists (VL) [98, 99, 119] and cell linked lists (CLLs) [98, 99, 120].

In the case of a VL, a list of neighbors is constructed within a potential cutoff distance R_c for each particle. Then, for a given particle, the energy computation (or the overlap check) is only performed for its precomputed neighbors. To avoid

reconstructing the VL after every MC step, a distance $\tilde{R}$ slightly larger than R_c is selected. Thus, although the asymptotic complexity is still $\mathcal{O}(N^2)$, the prefactor is much smaller compared to exhaustive particle pair computations. Moreover, complexity may be reduced by individually optimizing $\tilde{R}$ for each system [121].

CLLs also provide the means to compute interactions only in the neighborhood of a given particle, but instead of constructing a strict neighbor list, they are based on a bucket-sort algorithm. First, the simulation box is partitioned into a grid of cells whose heights are equal to or greater than R_c . Then, each particle is assigned to its corresponding cell. Now, when computing the interaction energy of this particle, only the neighbors belonging to $3 \times 3 \times 3$ surrounding grid cells must be taken into account. In MC simulations, the CLLs are usually rebuilt after each box move. Local particle-cell reassignments must also be performed after each accepted particle move. As the neighbor lookup is performed in constant time $\mathcal{O}(1)$, a single MC step using CLLs scales as $\mathcal{O}(N)$. CLLs can also be used to construct a VL with the same $\mathcal{O}(N)$ scaling. Combining CLLs and a VL may provide a prefactor speed-up when the construction of CLLs imposes a large overhead. In RAMPACK, usually less than 10% of the walltime is spent on building the CLLs, thus a VL is not used.

To maximize performance, CLLs must be implemented with care. For example, dynamically allocating the memory to store particles in each cell separately would increase the rate of cache trashing due to memory fragmentation. Fortunately, CLLs can be realized in a continuous, pre-allocated memory [122]. It is done by utilizing two main arrays:

- **Cell heads array** A flat array with the length corresponding to the number of grid cells. Each slot stores the index i of one of the particles in the cell – the “head” of the linked list (hence the name). Assuming that the grid has size $l_x \times l_y \times l_z$, the three-dimensional cell index (j_x, j_y, j_z) can be translated to the flattened index J using the formula $J = j_x + j_y l_x + j_z l_x l_y$.
- **Successor list** A flat array of length equal to the number of particles N . At index i (that is, for the i th particle), it contains the index of the next particle contained in the same cell.

All particles in a given cell can be iterated by first reading the CLL’s head from the cell heads array and then traversing the successor list. The end of the CLL (as well as an empty head) is marked by a special value (for example, -1), which cannot represent a valid particle index.

In principle, cells in the $3 \times 3 \times 3$ neighborhood can be identified by operations on cell indices. However, a significant performance boost may be achieved by pre-computing flat index shifts for neighboring cells. In order to do this, an additional flat array (cell mapping array) storing an $(l_x+2) \times (l_y+2) \times (l_z+2)$ grid is used [122]. Additional cells on each wall of the simulation box are the so-called *ghost cells*, which are PBC reflections of the cells on the opposite walls. All array slots, including those representing the ghost cells, contain the index of the corresponding cell in the original cell heads array. In such a construction, all neighboring cells may be iterated by performing constant index shifts in the cell mapping array.

This technique of realizing the CLLs is illustrated in Fig. 5.2(a).

CLLs may suffer from a severe performance drop when too many particles belong to the same grid cell. It is especially problematic for highly elongated particles. To mitigate the issue, RAMPACK allows one to partition anisotropic particles into smaller parts, which are stored as separate entries in CLLs. The number of partitions is a free parameter that should be optimized on a case-by-case basis.

5.1.4 Overlap detection

Regardless of how precisely the neighbors within a cutoff distance R_c are enumerated, the interaction energy between them must eventually be computed. For simple, soft potentials, such as Lennard-Jonnes, there is little room for improvement beyond minimizing the number of floating point operations and avoiding square roots. In contrast, for hard particles, which are the main topic of the articles [A.1-5], selecting a suboptimal intersection test can significantly hinder performance. Various overlap detection algorithms are broadly described in Ref. [123]. Here, only the ones used in the RAMPACK toolkit are briefly summarized.

RAMPACK currently supports the following shapes: spheres, spherocylinders, unions of spheres, unions of spherocylinders, and a broad class of convex shapes using the XenoCollide algorithm (which is discussed below). Spheres have the simplest intersection test – the distance between their centers must be compared to the sum of their radii. For the unions of spheres, the test must be repeated for all constituent parts. For spherocylinders, the overlap criterion is constructed in a similar manner – by computing the distance between two segments (spherocylinders’ heights) and comparing it with the sum of spherocylinder caps’ radii. The condition is the same in any number of dimensions, and an efficient implementation is described in Ref. [124].

The most versatile overlap test used in RAMPACK is the XenoCollide algorithm due to Snethen [125], which works for an arbitrary pair of convex, possibly different shapes. It is based on the concept of the so-called support function f_A . For a given direction $\hat{\mathbf{u}}$, f_A evaluates to a point $\mathbf{r}$ in a shape A , so that the dot product $\hat{\mathbf{u}} \cdot \mathbf{r}$ is the largest:

$$f_A(\hat{\mathbf{u}}) = \arg \max_{\mathbf{r} \in A} \hat{\mathbf{u}} \cdot \mathbf{r}. \quad (5.3)$$

To use the XenoCollide collision detection algorithm for shapes A and B , only two elements for each shape must be provided: the support functions f_A , f_B , and arbitrary points $\mathbf{p}_A$, $\mathbf{p}_B$ lying within the shapes. The rest is generic and does not require per-shape modifications of the algorithm. XenoCollide is based on the observation that A and B overlap if and only if their Minkowski difference⁴ $A - B$ contains the coordinate system origin $\mathbf{o}$. In subsequent iterations, the so-called *portal* is constructed and refined. The portal is a simplex (a segment for polygons and a triangle for polyhedra) with vertices that lie on the surface of $A - B$. If a

⁴Minkowski difference $A - B$ of two sets A and B is defined as $A - B = \{\mathbf{a} - \mathbf{b} : \mathbf{a} \in A, \mathbf{b} \in B\}$.

ray cast through $\mathbf{o}$ and $\mathbf{p}_A - \mathbf{p}_B$ intersects the portal, with $\mathbf{o}$ lying in the middle, an overlap is reported.

5.1.5 Parallelization

Performance on a single thread may be increased by choosing appropriate acceleration structures and, in the case of hard-core particles, fast overlap detection algorithms. Additional speed gains may be achieved by SIMD vectorization and optimization of memory utilization, such as coalesced access, promoting cache hits, and avoiding false sharing. However, as Moore's law hit a brick wall around 2005 [126], the CPU manufacturers shifted their focus to increasing the number of parallel cores on a single chip. Consequently, to utilize the full potential of modern architectures, parallelization schemes must be incorporated into high-throughput software.

In the NpT MC integration, during the box moves, one may simply parallelize energy calculations (or overlap checks) as they are independent. The problem arises for the particle moves. One may perform the moves in serial and use concurrent checks for overlaps with the neighbors, however, the overhead of assigning the tasks to a thread pool and synchronizing them may outweigh the performance gain. Thus, the moves themselves must be done in parallel, with appropriate care to avoid the race condition. Indeed, nearby particles cannot be perturbed simultaneously, as the data may be modified while another thread tries to read it.

Domain division

One of the solutions is the so-called domain division technique [127], which is used in RAMPACK. The simulation box is partitioned into a grid of identical domains, and each thread is assigned to exactly one of them. Then, the particle moves are performed in each domain separately, in parallel. To prevent data races⁵, one assigns areas (ghost layers) near the walls of the domains, where the particles are not allowed to move, with a width equal to or greater than the interaction cut-off radius R_c . Moreover, moves that transfer the particles from the active regions to the ghost layer are always rejected. The second part is crucial for maintaining a detailed balance condition. The concept is illustrated in Fig. 5.2(b). After every n cycles, the domains should be redefined so that the particles previously placed in the ghost layers can be perturbed. In RAMPACK, domains are redefined at the beginning of each new MC cycle.

OpenMP framework

Concurrency in the software is achieved through the OpenMP framework [128]. It is a simple compiler add-on (shipped by default with most modern C/C++ compilers), that is designed mainly to parallelize loops using simple `#pragma` directives. For example, domain division may be performed as in Lis. 5.1. The directive

⁵Data race happens when multiple threads modify a single memory location simultaneously without an imposed order of operations.

`#pragma ... collapse(3)` instructs OpenMP to unroll the three loops and invoke `perform_moves_in_domain(i, j, k)` concurrently in separate threads.

```
std::size_t numThreads = gridSize[0]*gridSize[1]*gridSize[2];

#pragma omp parallel for collapse(3) num_threads(numThreads)
for (std::size_t i = 0; i < gridSize[0]; i++)
    for (std::size_t j = 0; j < gridSize[1]; j++)
        for (std::size_t k = 0; k < gridSize[2]; k++)
            perform_moves_in_domain(i, j, k);
```

Listing 5.1: Possible implementation of the domain division technique using OpenMP. Here, `gridSize` stores the number of grid cells in each direction.

For loops with a larger number of iterations, OpenMP automatically distributes the work among the worker threads. For example, the computation of the total system energy may be parallelized⁶ as in Lis. 5.2. The work is divided in a way that minimizes the chances of false sharing.

```
double totalEnergy{};

#pragma omp parallel for num_threads(numThreads)
for (std::size_t i = 0; i < numParticles; i++) {
    for (j : get_neighbors_of(i)) {
        if (j >= i) continue; // avoid double counting
        totalEnergy += compute_energy_between(i, j);
    }
}
```

Listing 5.2: Possible parallelization of the total energy computation using OpenMP. The work is distributed among `numThreads` threads.

5.2 Software engineering

Maintaining a micro-scale code project (up to a couple thousand lines) usually does not require any special care beyond occasional manual testing. However, when the codebase grows larger, introducing modifications and fixing regression bugs can start to consume significant amounts of development time. Consequently, a systematic methodology must be introduced. The techniques of testing, maintaining, and expanding the software are topics of software engineering.

Software engineering emerged as a separate field in the 1960s [129]. It was a response to the ever-growing costs of developing and maintaining large codebases. The most notable example is IBM's OS/360 operating system. It was a decade-long project that, due to the lack of systematic development scheme, went significantly over time and budget [130].

⁶In RAMPACK, for box moves, energy computation and overlap counting is actually parallelized on the level of neighbor grid cells.

Until now, many so-called good practices and methodologies have been developed from which both smaller and larger projects may benefit. At this point, RAMPACK has around 40,000 lines of C++ code. This section summarizes some of the software engineering techniques used to ensure that the results produced by it are accurate while retaining low maintenance cost⁷.

5.2.1 Clean code

At the level of programming particular classes and functions, as well as larger components, there is a set of rules and recommendations that improve the quality of the code and make it easy to read, understand, and maintain. A code that meets these requirements is often called a *clean code*.

Most good coding practices were designed for object-oriented programming (OOP), as it repeatedly proved to be an efficient way of describing real-world problems. A classic literature devoted to effective OOP includes *Clean code* by RC Martin [131], *Design Patterns* by “The Gang of Four” [132], and *Refactoring* by M Fowler [133].

Four pillars of OOP

OOP is based on four main concepts, usually referred to as *four pillars of OOP*:

1. **Abstraction** The complexity may be hidden behind a simple API (application programming interface). In this way, complicated operations may be performed without a full understanding of the details by the caller. Abstraction layers are meant to gradually build a complex system from simpler blocks.
2. **Encapsulation** The use of private and protected fields and methods in classes hides the implementation details from the user and decreases a risk of putting an object into an invalid state.
3. **Inheritance** It enables one to arrange classes into a hierarchical structure. Derived classes may inherit fields and methods of their base classes. Nowadays, it is advised to prefer inheriting interfaces over implementations⁸.
4. **Polymorphism** This pillar is strongly connected with abstraction and inheritance. Instead of using concrete classes, one defines an interface with a desired API. Concrete implementations are provided by derived classes. It enables a high runtime flexibility.

The whole RAMPACK package is built around these concepts. For example, each type of shape, with underlying interactions and geometry, is a subclass of the `ShapeTraits` interface. Classes such as `Packing` and `Simulation` implementing MC integration do not explicitly calculate the interaction energy or perform an overlap check between particular pairs of shapes but delegate it to the concrete

⁷In this context, *cost* is associated with time needed for fixing bugs, as well as wasted CPU-hours on a computer cluster due to them.

⁸Extensive inheriting of implementations leads to many hidden dependencies, which facilitates error propagation.

implementation of the `ShapeTraits` interface. In this way, adding a new shape does not require modifying any MC integration routines.

SOLID

Robert C. Martin devised a set of five rules that lead to clean and easily maintainable code. Their first letters are organized into a SOLID acronym [134]. They are summarized below, with a note on how they were incorporated into RAMPACK's design.

1. **Single Responsibility Principle** Each interface or class should be responsible for a single, concise set of functionalities. In RAMPACK, there are separate classes encapsulating particular data structures and algorithms, for example, `ActiveDomain` and `DomainDecomposition` for the domain decomposition technique, or `ObservableCollector` gathering observable values during the simulation.
2. **Open-Closed Principle** Software entities should be open to extensions but closed to modifications. In other words, the systems ought to be designed in such a way that adding new functionality requires a minimal amount of modifications in the existing code. In RAMPACK, for example, adding a new observable can be done by writing a new subclass of `Observable` or `BulkObservable` and registering them in appropriate object factories. `ObservableCollector` class does not need to be modified or even recompiled.
3. **Liskov Substitution Principle** Any derived class should be able to be substituted in place of a base class without breaking the code. This leads to the so-called *design by contract*, where the user of an interface can make assumptions regarding the inputs and outputs of particular methods. For example, `ShapeGeometry` interface has methods returning primary (long) and secondary shape axes. The caller may assume that a correctly implemented subclass returns axes which are perpendicular.
4. **Interface Segregation Principle** Interfaces should be designed in such a way that all of their methods are often used together. This rule is violated when a single interface gathers many independent sets of methods, which introduces unnecessary dependencies to the code that uses only one of those sets. In RAMPACK, `ShapeTraits` is actually a collection of three interfaces: `Interaction` responsible for energy calculation and overlap detection, `ShapeGeometry` describing geometric properties of particles, such as a volume or shape axes, and a list of `ShapePrinter`-s responsible for representing the shape in a particular output format.
5. **Dependency Inversion Principle** Lower-level concrete mechanisms should depend on higher-level general policies, not vice versa. Higher-level abstraction layers present interfaces, which lower-level layers implement. In RAMPACK, for example, `Simulation` class exposes the `SimulationRecorder` interface, which is responsible for storing the trajectory. Lower-level classes implementing it, such as `RamtrjRecorder`, output a particular representation of the trajectory to a general `std::ostream` input-output stream. On

the lowest level, a concrete `std::fstream` object may then be used to save the trajectory to a file on a storage device.

Design patterns

Design patterns (DPs) are reusable schemes for writing code that provide ready solutions for frequently occurring problems. They were popularized by “The Gang of Four” (Gamma, Helm, Johnson, Vlissides) in their book [132]. Further literature includes Refs. [135, 136]. Although the DPs are a separate, self-contained entity, it is practical to regard them as a way of realizing more general principles, such as SOLID. Over the years, countless DPs were developed, both general (such as Factory or Observer) and language-specific (such as CRTP – Curiously Recurring Template Pattern – in C++).

RAMPACK uses a wide variety of DPs. Only a few, selected ones, are listed below, together with examples of how they were used:

1. **Builder pattern** The construction of a complicated, compound object is delegated to a separate class. In RAMPACK, `RampackParameters` structure contains a fully prepared set of objects (such as a concrete implementation of `ShapeTraits` or `ObservableCollector` with all observables set up). It is prepared based on the input file, which is fed to the PYON framework (see Sec. 5.3.1), acting as a Builder pattern.
2. **Decorator pattern** A new functionality is added to the object by enclosing it into another object with the same interface. An example from RAMPACK is the class `TruncatedPlayer` which encapsulates any `SimulationPlayer` used to restore a recorded trajectory, but truncates it to a preset length.
3. **Strategy pattern** A task used as a part of a larger process is extracted to a separate interface. This way, many alternative algorithms implementing this interface may be used interchangeably. In RAMPACK, many aspects of the MC integration, such as performing trial moves or dynamically varying thermodynamic parameters (temperature, pressure) are realized by abstract interfaces (`MoveSampler`, `TriclinicBoxScaler`, `DynamicParameter`), which may be used in any combination.

Miscellaneous guidelines

Apart from larger frameworks and concepts, there are numerous smaller and more specific guidelines that help to increase the quality of code. Some of them are gathered below.

- Descriptive names of symbols should be used (for example, `TricSc` is less specific than `TriclinicDeltaScaler`).
- One should prefer code comments describing motivations instead of behavior. If the code is readable, the behavior can be inferred directly from it.
- Functions should not be long or have excessive nesting and should have a single responsibility. In RAMPACK, most functions/methods are up to forty

lines long and up to three levels of nesting.

- DRY (Don't repeat yourself) – reoccurring code fragments should be extracted to separate functions. It helps reduce perceived complexity and facilitates debugging.
- The codebase should be frequently refactored. This means identifying parts with a poor structure and rearranging them. Refactoring techniques are extensively described in [133].
- One should use well-recognized, language-specific guidelines, such as Cpp Core Guidelines for C++ [137], or PEP for Python [138].

5.2.2 Testing

Testing is an inherent part of the development process. In computational science, a defective software may force the researcher to redo thousands of core-hours worth of simulations. Thus, the importance of detecting incorrect behavior as soon as possible cannot be overstated. Software testing emerged as a whole, separate branch of computer science. A prominent literature includes [139–141]. Testing techniques vary significantly in the extent of functionality they cover and in the degree of automation. This section will walk through all levels of testing employed in RAMPACK, starting from the lowest to the highest level of comprehensiveness.

Unit tests

Unit tests are tasked to test the most specific parts of the codebase, such as individual methods, classes, and modules. They are designed to run quickly, so they can be often invoked during the development process. Unit tests serve two main purposes:

1. They allow to test fragments of code in isolation from the rest of the software. It is especially useful when creating new functionality.
2. They act as regression tests. Namely, when changes to the codebase are made (for example, during the refactoring process), unit tests can detect newly introduced bugs in previously working modules. In addition, the source of the discrepancy is usually pinpointed with high precision.

For a given code unit, tests usually cover one or two normal use cases as well as the edge cases. It is often said that the number of test cases should be approximately equal to the number of linearly independent control flow paths (cyclomatic complexity) [142, 143]. In RAMPACK, a vast majority of classes is unit tested using *Catch2* testing framework [144], paired with *trompeloeil* [145] for creating mock objects⁹. For example, the tests for the **Packing** class verify the integrity of all operations, such as translations, rotations, box scaling, or accepting and rejecting moves. The operations are tested for both soft and hard potentials. Running a whole suite of unit tests takes under a second.

⁹Mock objects are procedurally created, programmable instances of a given interface, which can control which methods are called and how.

Validation tests

Some parts of the code, especially the stochastic ones, are not eligible for unit testing. Moreover, the integration of smaller parts into a whole system should also be verified. In RAMPACK, both issues are solved by performing a set of short MC simulations on a small number of particles and comparing the averages of selected observables (such as the packing fraction) with the values from the literature. Such a procedure validates the majority of the codebase at once. Validation tests must be carefully chosen and prepared. On one hand, they need to cover all important use cases – soft or hard potential, plain or compound particles, monodisperse or polydisperse systems, boxes with or without hard walls, etc. On the other hand, they should not take too long. Currently, the whole suite of validation needs around thirty seconds to complete. Consequently, likewise for the unit tests, they may be run on a regular basis.

End-to-end tests

The ultimate, end-to-end validation is done by performing real-world, research-scale simulations. The integrity of the software was verified on a set of basic shapes, such as spheres and spherocylinders, and basic soft potentials, such as Lennard-Jones. The results obtained in the articles [A.1-5] were cross-referenced with a similar research (for example [24, 49, 146]), and, in the case of [A.1], with independent MD simulation performed using the LAMMPS toolkit.

5.2.3 Open-source infrastructure

RAMPACK is an open-source project. This means the source code is publicly available, and anyone can contribute. It is hosted on *GitHub*, together with documentation and tutorials.

Semantic versioning

The project is versioned semantically [147, 148]. It means that the version number consists of three parts: major, minor, and patch. For example, for version number v1.2.3, the major version number is 1, the minor – 2, and the patch – 3. The patch number is increased when the update contains only bug fixes. The minor number is increased when new functionality is added without breaking the existing API. Finally, the major number is increased when API-breaking changes are applied.

Version control and branching model

RAMPACK uses the *git* version control system. A custom branching model, loosely based on *git-flow* [149], is employed (see Fig. 5.3). Only full, stable releases are merged into the `main` branch. Development takes place on two branches – `dev-minor` for new features and `dev-patch` for hotfixes. A patch release is performed by merging changes made in the branch `dev-patch` both into `main` and `dev-minor`. In case of a minor release, the changes made on the `dev-minor` branch are first merged into the `dev-patch` branch, and then the `dev-patch` branch is

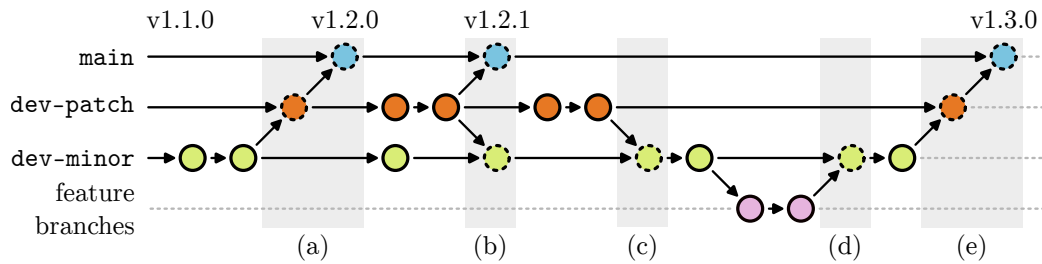


Figure 5.3: Illustration of the custom branching workflow used in RAMPACK. Commits are represented by circles. The circles on the same horizontal level, with identical colors, belong to the same branch. Branches are labeled on the left side (the lowest level – the gray dashed line – represents all feature branches). Arrows denote the timeline in the commit history. Circles with a dashed contour represent merge commits. We assume that starting from the left, the software is at version v1.1.0. Each merge to the **main** branch is equivalent to a new (minor or patch) release. Gray areas highlight various merging scenarios: (a) a minor release, where **dev-minor** is first merged to **dev-patch**, and then to **main**; (b) a hotfix (with patch release), where **dev-patch** is merged both to **dev-minor** and **main**; (c) a non-critical bugfix – **dev-patch** is merged only to **dev-minor**, without a new release; (d) a feature branch is merged into **dev-minor**; (e) another minor release.

merged into **dev-main**. The workflow was designed with three key assumptions in mind:

1. The **main** branch must always contain a stable release.
2. Hotfixes and new functionality should be developed in separate branches. In this way, critical bug patches from **dev-patch** can be applied before a new minor update is finalized on the **dev-minor** branch.
3. **main**, **dev-minor**, and **dev-patch** branches should remain flat on a branch graph, and merges should not intersect them. In this way, the visual tracking of changes is significantly simplified.

Larger new features may be developed on separate feature branches, which are then merged into **dev-minor**.

Continuous integration

Continuous integration (CI) is a mechanism that automatically verifies that the code currently hosted in a remote repository can be used to successfully build and execute the software. It is mainly achieved by running automated test suites on the changes pushed by the developers. RAMPACK uses *GitHub Actions* for CI. CI tasks are run on every push or pull request to **main**, **dev-minor**, and **dev-patch** branches. CI often involves performing other automated tasks, such as generating documentation or creating *git* tags. For example, RAMPACK's CI, apart from running unit and validation tests, detects malformed links in the user documentation.

Code documentation

```
/**
 * Computes the sum of two integers @a i1 and @a i2.
 * @param i1 first summand
 * @param i2 second summand
 * @return a sum of @a i1 and @a i2
 */
int add(int i1, int i2) {
    return i1 + i2;
}
```

Listing 5.3: *Doxygen* documentation of a toy function computing a sum of two integers.

Providing source code API documentation helps new contributors to learn how the software is structured and what are the responsibilities of particular modules. Moreover, it is also useful for more experienced contributors when they revisit old code fragments. In RAMPACK, the documentation is kept with the code itself, using specially formatted comments, which can be applied, among others, to functions, methods, and classes. An example is shown in Lis. 5.3. The *Doxygen* tool [150] can then be used to traverse the source tree and generate interactive documentation for it in various formats, such as HTML or $\text{\LaTeX}$.

5.3 User interface

Reusable scientific software should have a convenient, flexible, and intuitive user interface. A well-considered design can significantly reduce the time required to configure and debug simulations. As mentioned in previous sections, RAMPACK is currently distributed as a single binary, which can be used to perform the MC sampling and basic data analysis. It is a command-line tool with several modes and an array of options that alter the software’s behavior. MC runs are programmed using input scripts. The next sections describe the format of the input scripts as well as summarize the command-line utilities. The full documentation of all aspects of the user interface is available at

→ <https://github.com/PKua007/rampack/blob/main/docs/reference.md>.

5.3.1 PYON format

When choosing the format in which the input files should be written, the following goals were set:

1. It should be intuitive and easily readable.
2. It should be concise.
3. It should be familiar to most researchers.

4. It should reflect the object-oriented design of the software and be easily parsed to RAMPACK's internal representation.

Many standard formats were considered, but neither of them fulfilled all of the above requirements. The list, together with an argumentation, includes:

- **INI** It is a simple configuration file with key-value pairs and sections. It is very simple and intuitive; however, nesting, which is needed to reflect the structure of objects, cannot be easily achieved.
- **XML** This format is a common choice for configuration files with easily realized nesting. However, it is verbose and inconvenient for inexperienced programmers.
- **JSON** The format is mainly used for data serialization. High nesting significantly decreases readability.
- **YAML** YAML was the best candidate of all the standardized ones that were considered. It is designed to be concise and human-readable, with a selection of common data structures. However, prototyping showed that representing objects in this format is not sufficiently compact and intuitive.

```
rampack(
    version = "1.0",
    shape = sphere(r=0.5),
    arrangement = lattice(cell=sc, box_dim=15, n_shapes=1000),
    temperature = 1,
    pressure = 11.5,
    move_types = [translation(step=1)],
    box_move_type = delta_v(step=10),
    seed = 1234,
    handle_signals = True,
    runs = [
        integration(
            run_name = "liquid",
            thermalization_cycles = 500000,
            averaging_cycles = None,
            snapshot_every = 1000,
            output_last_snapshot = [ramsnap("packing_liquid.ramsnap")],
            record_trajectory = [ramtrj("recording_liquid.ramtrj")]
        )
    ]
)
```

Listing 5.4: An example PYON configuration file for an NpT liquid of hard spheres.

Consequently, a custom PYON format was designed. Its name stands for **PY**thon **O**bject **N**otation, as it is largely based on Python's syntax. Thus, even though the PYON format is specific to the RAMPACK package, most researchers using Python should understand it easily. PYON supports most standard Python primitives and structures, such as integer and floating-point numbers, strings, arrays, dictionaries, booleans, `None`, and, most importantly, objects (called data-classes). Lis. 5.4 shows an example input file of an NpT simulation of hard spheres

in a liquid state. Please note that the snippet resembles creating a nested object structure, with `rampack` object at the top, which was one of the design goals. This format closely models the actual object tree in the software. Object constructors have an analogous behavior to the Python language. One may use positional and keyword arguments, as well as their mixtures. Variadic positional and keyword arguments are also supported.

```

struct Person {
    std::string name;
    std::string surname;
    int age;
};

auto personMatcher = MatcherDataclass("person")
    .arguments({{"name", MatcherString{}.nonEmpty()},
               {"surname", MatcherString{}.nonEmpty()},
               {"age", MatcherInt{}.positive().mapTo<int>()}})
    .mapTo([](const DataclassData &person) {
        Person personOut{};
        personOut.name = person["name"].as<std::string>();
        personOut.surname = person["surname"].as<std::string>();
        personOut.age = person["age"].as<int>();
        return personOut;
    });

```

Listing 5.5: An example PYON matcher for the `Person` structure. It requires nonempty name and surname, as well as positive integer age. It will match, for example, the following snippet: `person("John", age=45, surname="Smith")`. Please note that `"John"` is parsed as the first positional argument (name), while the rest of the arguments are given in keyword form in an arbitrary order.

To handle the PYON format, a custom framework was developed. First, the abstract syntax tree (AST) is created from the input file using a simple recursive descent parser [151]. Then, AST needs to be interpreted. It is done by the so-called *matchers*, which directly translate PYON primitives, data structures, and objects into RAMPACK's internal representations of them. The matchers are written individually for particular components and rely heavily on C++11 lambda expressions. An example matcher is shown in Lis. 5.5.

5.3.2 Command line

RAMPACK executable (`rampack`) groups its functionality into several modes¹⁰, in a similar fashion to *git*. Each mode has a specific set of command line options that modify its behavior¹¹. Moreover, RAMPACK comes with tab-completion scripts for *bash* and *zsh* shells. The following is a short summary of the modes available in the software. A given mode is invoked by executing `rampack [mode name]`.

¹⁰The available modes can be listed by executing `rampack --help`.

¹¹The options can be listed by executing `rampack [mode name] --help`.

<code>casino</code> ¹²	The main mode responsible for MC sampling. The PYON configuration is read from the file passed as an argument of the <code>-i</code> option. Other options can be used to, for example, resume interrupted runs, redirect standard output to a file, or change logging verbosity.
<code>preview</code>	This mode can generate a preview of the initial configuration from the input file in any of the supported snapshot formats. It is especially useful for designing lattices with a custom unit cell or if one performs complex lattice transformations. In such cases, it enables one to quickly verify the specification.
<code>shape-preview</code>	Auxiliary tool to list shape data (such as volume, axes, interaction centers, etc.) as well as to output its 3D model to an external file.
<code>trajectory</code>	Data analysis mode processing recorded simulation trajectories. It supports various tasks through command-line options, such as truncating the trajectory, exporting it to another format, averaging observables, previewing snapshots, and more.

5.4 Performance

The final section is devoted to RAMPACK's performance, mainly in relation to its scaling with the number of concurrent threads. The performance of a multi-threaded application may be bottlenecked by multiple factors, including

- serial parts of the code, i.e., the ones that cannot be parallelized;
- thread synchronization – one thread may be forced to wait until the lock is released by another thread;
- critical sections – regions of parallelized code, which can be entered only by a single thread;
- thread divergence – some of the threads may finish their task earlier than others, and thus they must idle;
- memory-bound code – scaling to a higher number of threads may be bottlenecked by RAM's bandwidth.

In RAMPACK, there are very few critical sections and explicit thread barriers. The workload is well-balanced among all the threads. However, there are parts of the code that can be parallelized only partially, such as adding interaction centers to the neighbor grid or performing domain division. As long as their contribution

¹²The mode's name *casino* refers to the Monte Carlo casino in Monaco, where Ulam's (one of the creators of MC methods) uncle often used to play. MC methods were named after the same gambling facility.

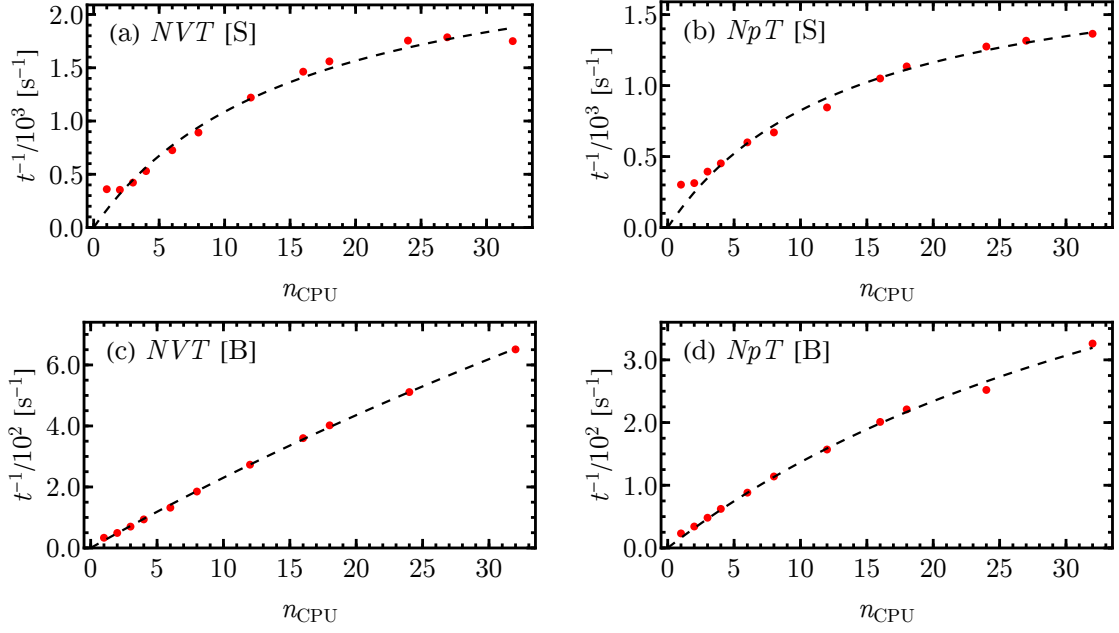


Figure 5.4: MC sampling performance (measured in a number of full MC cycles per second t^{-1}) as a function of the number of CPU cores n_{CPU} for a system of hard spheres [S] and banana-shaped particles built of hard spheres [B], both in NVT and NpT ensembles. Red points are the measurements, while the black dashed line is a numerical fit $t = t_s + t_p/n_{\text{CPU}}$. (a) NVT spheres with $t_p/t_s \approx 16$, (b) NpT spheres with $t_p/t_s \approx 14$, (c) NpT bananas with $t_p/t_s \approx 160$, and (d) NpT bananas with $t_p/t_s \approx 49$.

to the walltime is small, the performance drop is negligible. It becomes problematic mainly for simple interaction potentials and a large number of concurrent threads.

To measure the scaling quantitatively, two systems were benchmarked: 9000 hard spheres (packing fraction $\eta \approx 0.49$), and 19200 banana-shaped particles built of nine hard spheres ($\eta \approx 0.43$) – the same shape as in [A.2]. Both were simulated in the NVT and NpT ensembles on a machine equipped with an AMD Ryzen Threadripper Pro 5975X 32-core CPU. The scaling was measured for a different number n_{CPU} of CPUs used, ranging from $n_{\text{CPU}} = 1$ to $n_{\text{CPU}} = 32$. Hyperthreading, enabling one to run two threads on one physical core, was also tested; however, the performance boost was negligible, and thus it will not be discussed further.

The results of the measurements are shown in Fig. 5.4. There, t is the time needed to perform a full MC cycle, and, consequently, t^{-1} is the number of cycles per second. For the spheres [Fig. 5.4(a, b)], there is no performance boost when two cores are used instead of one. This is probably due to the need to employ new structures, such as domain division in the parallel code, which introduces additional overhead. Parts of those structures are also parallelized; thus, using more than two cores gives a visible overall speed-up until around $n_{\text{CPU}} = 16$, where t^{-1} reaches a plateau. Qualitatively, the NVT and NpT systems are comparable; however, the scaling in the case of NpT is slightly worse. Bananas [Fig. 5.4(c, d)] have a much better scaling. There, the speed-up is already visible for two cores and grows almost linearly up to a maximum number of cores $n_{\text{CPU}} = 32$ tested.

The overlap criterion for the bananas is more complex than the one for spheres. Thus, more time is spent in parts of the code that parallelize well.

To model the $t^{-1}(n_{\text{CPU}})$ dependence, we assume that the time t spent on realizing a single cycle consists solely of a code that is independent of n_{CPU} (a serial code), executing for time t_s , and a parallel code with an ideal scaling, executing for t_p/n_{CPU} . Consequently,

$$t = t_s + t_p/n_{\text{CPU}}. \quad (5.4)$$

The ratio t_p/t_s measures how parallelizable the code is, i.e., it is the number of cores for which serial and parallel parts have a similar duration. It gives a rough estimate of the maximal value of n_{CPU} , after which the performance gain is disproportional to the additional power consumption.

The fits of Eq. (5.4) in Fig. 5.4 are represented by black dashed lines, and the values of t_p/t_s are given in the caption. The best scaling is achieved for the NVT sampling of bananas, which scales well up to $n_{\text{CPU}} = 32$ according to the measurements, and over $n_{\text{CPU}} = 100$ according to the extrapolation. The scaling worsens in the NpT ensemble, probably due to partially serial rebuilding of the neighbor grid during the box moves (the neighbor grid contains $9 \times 19200 = 172800$ interaction centers). For spheres, the fits confirm that it is wasteful to use more than $n_{\text{CPU}} = 16$ cores.

It is important to note that parallelized software always has a varying degree of serial overhead. Thus, if possible, it is better to run many independent simulations on a smaller number of CPUs each. However, if the system is large, a low core count can make the simulation too slow to be used in a meaningful way. Thus, high parallelization is sometimes necessary to achieve scientific goals. Using multinode computation (distributing the work among multiple nodes of a computing cluster) enables the simulation of hundreds of thousands or even millions of particles, which is necessary to observe some long-range effects [152, 153]. Massive parallelization can be realized via GPGPU. Thus, support for MPI and GPU acceleration is planned in a future release of RAMPACK.

Finally, the performance of RAMPACK was compared with HOOMD-blue [114] and LAMMPS [113]. The comparison with HOOMD-blue was straightforward. The results of Ref. [105] for dodecahedra on a single thread were compared with an identical system in RAMPACK, where the latter software achieved around 50% performance of the former one on a machine with a similar CPU. As LAMMPS is an MD software, support for hard potentials is limited. However, steric interactions are often modeled using the purely repulsive WCA potential¹³. Thus, a four-thread performance comparison was made for a system of rigid bananas built of 11 beads (the same as in [A.1-2]), interacting via the WCA potential in LAMMPS simulations and hard-core in RAMPACK simulations. The number of timesteps per second in LAMMPS and the number of MC cycles per second in RAMPACK were comparable. Thus, RAMPACK's performance for a moderate number of threads is comparable to or slightly worse than that of well-established software toolkits.

¹³WCA potential, for a distance r between interaction centers, is defined as $U(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6] + \epsilon$ for $r \leq 2^{1/6}\sigma$ and $U(r) = 0$ elsewhere ($\epsilon, \sigma > 0$ are parameters).

Chapter 6

Articles

Summary

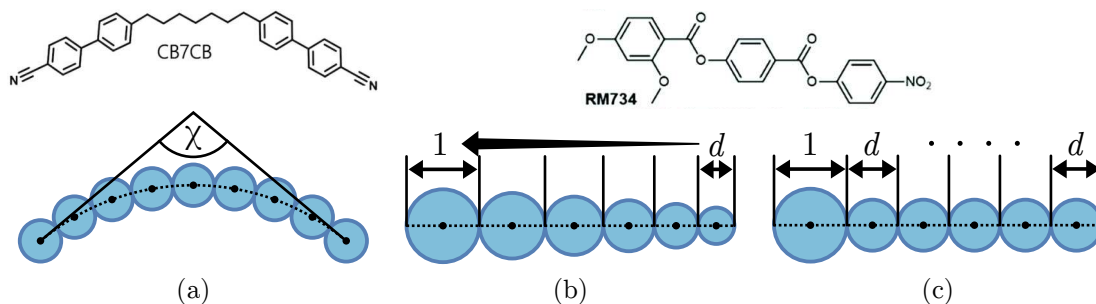


Figure 6.1: Particle models used in [A.1-5] studies. (a) Top: banana-shaped CB7CB molecule, which forms the N_{TB} phase in the experiment. Reprinted from Ref. [154] with the permission of Optica Publishing Group. Bottom: particle model used in the studies [A.1-2]. It consists of n tangent spheres with their centers placed on a circular arc, parameterized by the angle χ between two lines tangent to the arc at the points coinciding with the centers of two endpoint spheres. (b, c) Top: conical RM743 particle, for which N_F was experimentally observed. Reprinted from Ref. [23] with the permission of the Royal Society of Chemistry. Bottom: two hard-sphere models of RM743. There, (b) shows the taper built of n colinear, tangent spheres with linearly increasing diameters from d (a free parameter) to 1. The model was used in [A.3, A.4]. Panel (c) presents the lollipop model, similar to (b), with, however, different radii: $n - 1$ spheres with radius d , and a single sphere with radius 1 at one of the ends. This shape was studied in [A.5].

The main Chapter of the Thesis gathers a series of articles [A.1-5] that, through MC simulation, investigate the phases formed in systems of hard-core particles, with either a transversal [A.1-2] [Fig. 6.1(a)] or longitudinal [A.3-5] [Fig. 6.1(b, c)] deformation. As postulated by Meyer [60] and further supported by de Gregorio *et al.* [59], such shapes should promote, respectively, bend and splay deformation modes. The purpose of the articles [A.1-5] was to assess how important the shape effect is in promoting phases with a nonstandard symmetry. The following is a short summary of the findings.

Bent-core systems

Articles [A.1-2] consider bent-core systems modeled by hard-core banana-shaped particles consisting of hard spheres [Fig. 6.1(a)]. Ref. [A.1] studies the system with a constant number of particles $n = 11$ and a varied bend angle χ , expanding on the seminal work of Greco *et al.* [24], which, for the first time, confirmed that the N_{TB} phase can be formed in a purely entropic system. Our work pinpoints the exact area in the (η, χ) phase space (where η is the packing fraction), where N_{TB} can be observed. That is, it appears below $\chi \approx 135^\circ$ and spans the packing fractions $\eta \in [0.29, 0.35]$. It is formed directly over the Iso phase ($\chi > 113^\circ$) or follows the Iso- N - N_{TB} phase sequence ($\chi < 113^\circ$). In particular, Greco studied the system with $\chi = 130^\circ$, while for $\chi \approx 122^\circ$ one restores the proportions of CB7CB [155]. Systems with $\chi < 90^\circ$ were not considered, as particles with acute bend angles do not form the N_{TB} phase in the experiment.

Above N_{TB} , the Sm_{SB} polar phase is assembled. This contrasts the uniform nematic range ($\chi > 135^\circ$), over which a standard type A smectic is observed. The Sm_{SB} phase was also reported by Chiappini and Dijkstra [49] in a similar study on bent spherocylinders. For η values in the smectic range and angles $\chi < 130^\circ$, we discovered another SmX smectic with polarization splay. However, its exact form has not been scrutinized until the next study [A.2].

The article [A.2] provides further insight into the model. There, instead of scanning different values of χ , the parameter remains constant at $\chi = 130^\circ$, while the number of beads n changes in the range $n \in [7, 15]$. This emulates varying the length (or thickness) of the particle. The N_{TB} phase is stable for all $n \geq 10$ with a range of packing fractions that drifts from $\eta \in [0.33, 0.36]$ for $n = 10$ to $\eta \in [0.24, 0.32]$ for $n = 15$. In other words, the range of N_{TB} widens and moves to lower η values when the molecular length is increased. For $n < 10$, N_{TB} is replaced by SmA . Over N_{TB} and partially over SmA , Sm_{SB} is observed. Interestingly, the SmX phase from [A.1] is recreated for $n \leq 13$, in the packing fraction range $\eta \in [0.40, 0.43]$. Contrary to [A.1], the article [A.2] fully identified SmX as a variant of B_1 , which is one of many so-called banana phases, often observed in bent-core systems [156].

In conclusion, the N_{TB} phase can be formed in purely entropic systems without the help of additional interactions. Importantly, it appears not only for a specific particle but is observed in quite a wide range of shape parameters, provided that the bend angle and the particle's thickness are small enough. Moreover, it is often accompanied by other nontypical phases, such as Sm_{SB} or B_1 .

Conical systems

Conical systems, consisting of linear particles with broken up-down symmetry, are a topic of the articles [A.3-5], where [A.3, A.4] consider tapers [Fig. 6.1(b)], and [A.5] is devoted to lollipops [Fig. 6.1(c)]. Once again, the interactions are hard-core. The motivation is ferroelectric N_F and splay N_S nematic phases, which were recently reported in the experiment [16, 19, 20] for different molecules, including RM734 (N_F) and DIO (N_F, N_S). Both molecules are characterized by a conical shape and a large molecular dipole moment. Currently, those two factors are

believed to be substantial for the formation of the novel nematic phases. The goal of our studies [A.3-5] was to assess whether nontrivial effects can be observed in purely entropic systems without the help of dipolar interactions.

Tapers with $n = 6$ and varying $d \in [0.4, 1.0]$ [see Fig. 6.1(b)], with proportions modeling RM743 and DIO molecules, are a topic of [A.4]. There, only standard liquid crystalline phases – N and SmA – are observed in the entire range of d under consideration. Although some polarization and splay order appear for the densest smectics, it is only local. The presence of ordered clusters suggests that a polar phase may exist nearby. In fact, three non-trivial polar phases are formed after crystalization: ferroelectric double-splay crystal ($\text{Cr}_{\text{DS}}\text{P}_{\text{F}}$), antiferroelectric double-splay crystal ($\text{Cr}_{\text{DS}}\text{P}_{\text{A}}$), and antiferroelectric splay crystal ($\text{Cr}_{\text{S}}\text{P}_{\text{A}}$). In particular, those structures resemble the single- and double-splay N_{S} variants proposed by Rosseto and Selinger [84]. The [A.4] study confirms that the splay and polarization order is promoted in the system; however, it requires high packing fractions η , which escape the range of liquids.

The numerical findings are supported by the DFT calculations (more precisely, the bifurcation analysis). A perfect nematic order was assumed; thus, splay deformations are not modeled. The DFT confirms the lack of the N_{F} phase in the system. Interdigitated smectic SmA_{d} (which is discussed in [A.5]) was also considered. The supposed N- SmA_{d} phase boundary almost overlaps the N-SmA phase boundary; however, the latter is the one actually realized in the computer simulations.

Importantly, de Gregorio *et al.* [59] predicted, by means of DFT calculations, that a long-range splay order should appear in a hard-core system of particles such as in Fig. 6.1(b), with $n = 11$ and $d = 1.22/0.78$. Such shapes are considered in the article [A.3]. We established that their system shows Iso-N-SmA- $\text{Cr}_{\text{DS}}\text{P}_{\text{F}}$ phase sequence. In particular, long-range polarization or splay order are lacking, although, once again, local correlations are present. We suggested that the most probable reason for the contradiction between DFT calculations and numerical simulations may be not including density modulation in the DFT model.

Finally, the article [A.5] considers an alternative model of a conical molecule, the lollipop [see Fig. 6.1(c)], with $d \in [0.4, 1.0]$. Similarly to the tapers, the N_{F} and N_{S} phases are absent. On the other hand, an array of non-standard, dense phases is observed. Two of them are interdigitated smectics: SmA_{d} and SmC_{d} . The interdigitated smectic is built of two superimposed oppositely polarized ferroelectric smectics, with a slight separation between the density maxima. We also observed an interdigitated bcc crystal (bcc_{d}) for $d = 0.85$. For $d \in [0.65, 0.8]$, an intriguing, globally isotropic phase appears, where local double-twist clusters are formed. We called it the isotropic double-twisted cluster liquid (Iso_{DT}).

In summary, the results suggest that entropic interactions alone are not enough to promote long-range splay or polar order. Consequently, the inclusion of strong dipolar moments appears to be necessary. However, conical systems display a richness of different liquid and crystalline phases, strongly depending on the details of the particle's shape.



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In silico study of liquid crystalline phases formed by bent-shaped molecules with excluded volume type interactions

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ABSTRACT

What impact does the mesogens' shape have on the formation of the liquid crystalline phase? Using Monte Carlo and molecular dynamics simulations we numerically studied a liquid composed of achiral, bent-shaped molecules built of tangent spheres. The system is known to spontaneously break mirror symmetry, as it forms a macroscopically chiral, twist-bend nematic phase [Phys. Rev. Lett. **115**, 147801 (2015)]. We examined a full phase diagram by altering the molecules' curvature along with packing fractions and observed several phases characterized by the orientational and/or translational ordering of molecules. Apart from conventional nematic, smectic A, and the aforementioned twist-bend nematic phase, we identified splay-bend smectic phase. For large densities and strongly curved molecules, another smectic phase emerged, where the polarization vector rotates within a single smectic layer.

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1. Introduction

Comprehension of the spontaneous mirror symmetry breaking (SMSB) phenomenon is essential for understanding fundamental aspects such as life itself [1–3]. Investigations revolving around the origins and corollary of SMSB stand simultaneously at the forefront and frontiers of contemporary soft matter science [4,5]. One of the playgrounds to investigate the nature of SMSB are liquid crystals (LCs), where supramolecular chiral and polar structures are assembled from achiral, bent-shaped (curved) molecules [6,7]. Bent-shaped molecules (BSMs) tend to form various phases, including smectics and nematics [8–10]. The latter, however, has recently experienced a resurgence of worldwide interest. It happened because of the discovery of twist-bend nematic (N_{TB}) phase [11–14], which constitutes the first example of SMSB in a liquid state with no support from long-range spatial ordering. The characteristic feature of N_{TB} is the emergence of heliconical (1D modulated) structure of nanoscale pitch ($p \approx 8 - 10$ nm) with a ground-state exhibiting a degenerate sign of chirality (ambidextrous chirality), which means that both helix handedness, either right or left, are equiprobable (Fig. 1). In no time, it turned out that one of the essential prerequisites for the stabilization of N_{TB} are “ade-

quately curved” molecules [15–17] in line with Meyer's [18] and Dozov's [19] conjecture. However, there is still an ongoing debate concerning the N_{TB} 's structure and properties [20,21]. Further advances in the studies of N_{TB} subsequently sprouted into a broad sub-field of liquid crystal research dedicated to novel nematic phases of non-standard symmetries [22–25].

It is noteworthy to point out that remarkable features of nematic phases formed by BSMs are not limited solely to the phenomenon of SMSB. The list is vast but just to name a few [29,9]: unusual hierarchy of elastic constants, giant flexoelectricity, non-standard dielectric, and rheological behaviours. The BSMs are also said to be the perfect candidates for optically biaxial liquid, namely biaxial nematic (N_B), predicted by Freiser in 1970 [30]. They owe it to the introduction of the “kink” in the molecular structure which naturally specifies a secondary direction perpendicular to the long molecular axis, for orientational ordering [31,32].

All the above makes LCs formed by BSMs, *per se*, a riveting field to explore both from experimental and theoretical points of view (see, e.g., [33–36,9,37,27,28] and references therein). In particular, substantial efforts were undertaken to decipher how the molecule's structure influences the emergence of individual mesophases [38,39,32]. One of valuable tools in such studies are computer simulations, such as Monte Carlo (MC) sampling and Molecular Dynamics (MD), which have a long-standing tradition in the investigation of structural properties of LC phases using a diverse range of models ranging from simplified lattice systems

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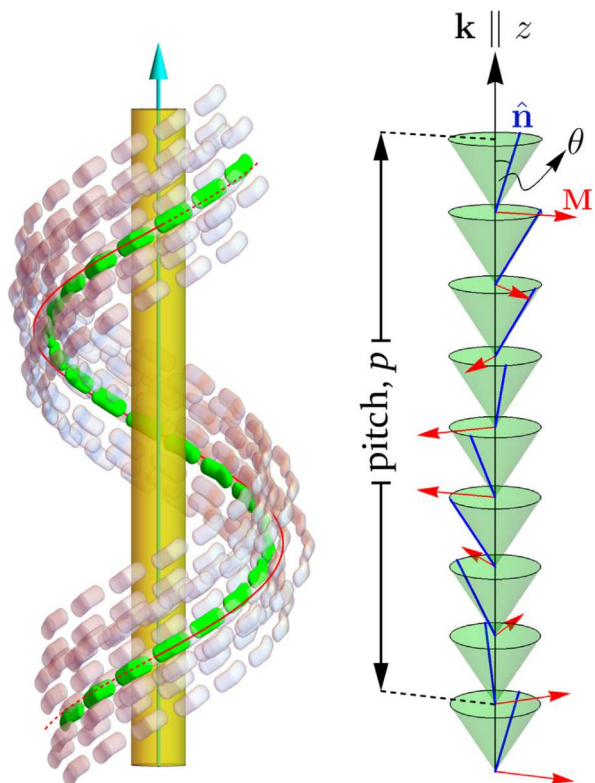


Fig. 1. Schematic depiction of the twist-bend nematic phase characterized by the finite pitch p and helicoidal tilt angle θ ($0 < \theta < \pi/2$) between the director $\hat{n}$ and the wavevector $\mathbf{k} \parallel z$ ($\mathbf{k} = k\hat{z} = (2\pi/p)\hat{z}$). The polarization $\mathbf{M}$, where $\mathbf{M} \parallel \hat{n} \times \mathbf{k}$, is precessing around $\mathbf{k}$ along with $\hat{n}$. Spontaneous mirror symmetry breaking in the twist-bend nematic phase, arising from chiral conformations of achiral molecules (ones lacking stereogenic center), leads to the ground-state with doubly degenerate handedness. Namely, each chiral conformer has its mirror counterpart differing in sign of chirality, which results in twin domains of opposite (left- and right-) handedness [26,16]. (Left) Adapted from Ref. [27] with permission from the Royal Society of Chemistry. (Right) Adapted from Ref. [28] published under ACS AuthorChoice with CC-BY license.

to fully atomistic ones [40–42]. Generally, but not limited to, the anisotropic shape of BSMs can be approximated in the simulations either by V-like or C-like shaped objects (reflecting the C_{2v} symmetry) composed of, e.g., needles [43–45], spheres [46–50], or spherocylinders [51–56]. It has been shown that those systems, each one separately, produce a richness of interesting nematic and smectic phases. However, especially appealing are the systems where the supramolecular chirality emerges out of pure entropy-driven interactions [49,57]. To our best knowledge, there is a modest number of works focused on computer simulations of N_{TB} and its structurally-related counterparts [58,59,13,49,55,56,60–62].

Herein, we extended the work of Greco and Ferrarini [49] where it was shown that for a model system of BSMs, composed of eleven tangent spheres (see Fig. 2), it is possible to observe the stabilization of N_{TB} arising from the packing entropy in MD simulations. We aim to provide an in-depth analysis of this system by altering the BSMs' curvature and packing fractions in order to obtain the full phase diagram for the liquid state¹. To achieve it, we performed both MC and MD simulations.

The article is organized as follows. In Section 2 the system under study is described together with the details concerning the

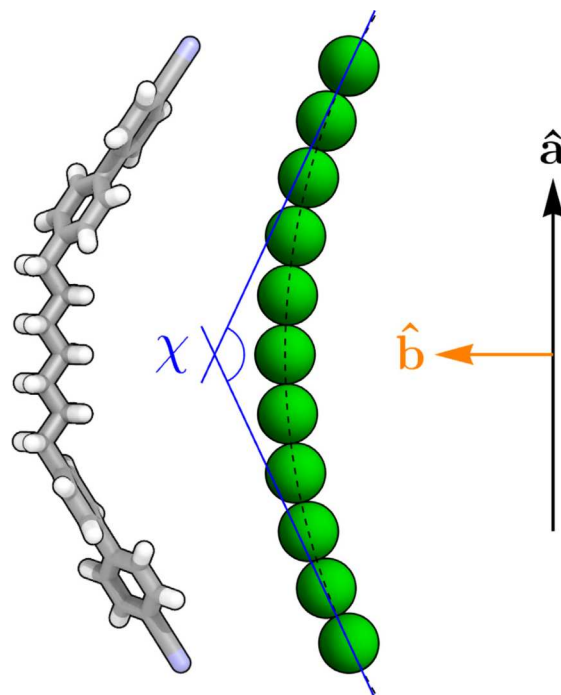


Fig. 2. Left: Molecular structure of N_{TB} forming mesogen CB7CB [11] rendered via QuteMol [63]. Right: Model bent-shaped molecule with C_{2v} symmetry composed of eleven tangent spheres whose centers are equidistantly distributed on the arc. The bend angle χ is defined as the angle formed by two lines, tangent to the arc at the centers of end-point spheres. Please note that in this convention, the higher the bend angle, the smaller is molecule's curvature (it is less bent). Unit vectors $\hat{a}$ and $\hat{b}$ define the molecular reference frame, where $\hat{a}$ equates with the molecular long axis and $\hat{b}$ is parallel to the molecule's twofold (C_2) symmetry axis.

MC and MD simulations used to investigate its properties. The results of the simulations are given in Section 3 where they are compared with the current literature. In Section 4 we provide conclusions drawn from the acquired data.

2. Model and simulation details

2.1. The model system

BSMs were modeled by eleven tangent spheres of diameter σ placed on a circular arc with a variable bend angle χ (see Fig. 2). For $\chi = 180^\circ$, the molecule reduces to a linear chain of tangent spheres, while for $\chi = 0^\circ$ it forms a semi-circle. To study lyotropic phase transitions in a system composed of such molecules, we examined two types of excluded-volume interaction. The first one is hard-core interaction [64], while the second is Weeks-Chandler-Andersen (WCA) [65,66] soft repulsion, defined as

$$U(r_{mn}) = \begin{cases} 4\epsilon \left[\left(\frac{\sigma}{r_{mn}} \right)^{12} - \left(\frac{\sigma}{r_{mn}} \right)^6 \right] + \epsilon & \text{if } r_{mn} < 2^{1/6}\sigma \\ 0 & \text{if } r_{mn} \geq 2^{1/6}\sigma, \end{cases} \quad (1)$$

where r_{mn} is the distance between the interaction centers and ϵ is the energy scale. The free parameters of the model (σ , ϵ) can be conveniently incorporated into the reduced pressure $P^* = P\sigma^3/\epsilon$ and reduced temperature $T^* = k_B T/\epsilon$. For hard-core repulsion, the equation of state depends only on a single parameter – the $P^*/T^* = P\sigma^3/(k_B T)$ ratio [67,64]. For WCA interaction the system is sensitive to P^* changes, while the dependence on T^* is weak [68]. The emergent phases were studied as a function of bend angle χ

¹ The study of regions, where crystal structures emerge is outside of the article's scope and stands as the starting point for further research.

and packing fraction η . The latter is a natural parameter for lyotropic systems and enables us to compare the two interaction models [68]. For both of them, the main contribution to Helmholtz free energy is the packing entropy: $F \approx -TS$ (the formula is exact for hard-core repulsion), so the phases with the highest entropy minimize F and thus are promoted.

2.2. Simulation methods

The hard-core interactions were simulated using Monte Carlo sampling in NPT ensemble [69] for $P^*/T^* \in [0.2, 2.0]$. The system was built of $N = 3000$ molecules. For a selected set of parameters giving periodic phases, simulation was repeated for $N = 6000$ and double the box size to ensure that the finite size effects are not present. A single MC cycle consisted of N molecule moves and a volume move. To perform a molecule move, a single molecule was sampled at random. Then, the molecule was translated by a random vector and rotated by a random angle around a random axis. The move was accepted provided it did not introduce an intersection. For volume moves all three lengths of an orthorhombic simulation box with periodic boundary conditions and the positions of molecules were scaled by three independent logarithmically distributed factors. Moves introducing overlaps were rejected and the rest of them was accepted according to Metropolis criterion. Anisotropic scaling was chosen to avoid frustration, which could introduce a bias in the period of emergent structures. The extents of random moves were selected such that the acceptance ratio was around 15%. The initial configuration was a diluted antiferroelectric sc crystal, which was then compressed or expanded to a target density. The equilibration was very sluggish due to the concavities of molecules and required up to 2×10^8 of full MC cycles. The production runs to sample ensemble averages consisted of 3×10^7 cycles. To accelerate the simulations, we parallelized them using domain division [70].

The MD simulations of $N = 2025$ molecules, interacting via the WCA potential in the NPT ensemble at various values of the pressure P^* in the interval $0.2 \leq P^* \leq 2.0$, were performed using the open-source software LAMMPS [71]. All relevant simulation aspects were set up according to the framework provided in [72]. Equilibration and production runs were conducted for 10^7 time-steps each.

Within both simulation schemes, i.e., MC and MD, we examined particles with a fixed bend angle $\chi \in [90^\circ, 180^\circ]$.

2.3. Order parameters

Distinctive features of a particular phase can be characterized by appropriate order parameters and the corresponding degree of ordering. In nematic and smectic phases, the molecules' long axes (denoted as $\hat{\mathbf{a}}$, see Fig. 2) tend to orient, on average, along a preferred direction called the director $\hat{\mathbf{n}}$ ($\hat{\mathbf{n}}^2 = 1$) [73]. Such kind of alignment can be quantified by the second-rank order parameter [74]:

$$\langle P_2 \rangle = \frac{1}{N} \left\langle \sum_{i=1}^N P_2(\hat{\mathbf{a}}_i \cdot \hat{\mathbf{n}}) \right\rangle, \quad (2)$$

where the sum is over all N molecules in the system, $P_2(\dots)$ is the Legendre polynomial of degree 2, $\hat{\mathbf{a}}_i$ is a molecular axis vector of i -th molecule (cf. Fig. 2) and $\langle \dots \rangle$ denotes the time average over uncorrelated system snapshots. If $\langle P_2 \rangle = 0$ orientations are isotropic, $\langle P_2 \rangle = 1$ is a perfect order, and for $\langle P_2 \rangle = -1/2$ all molecules are perpendicular to $\hat{\mathbf{n}}$. Alternatively, $\langle P_2 \rangle$ can be computed by diagonalising the second rank $\mathbf{Q}$ -tensor [74]

$$Q_{\alpha\beta} = \frac{1}{N} \sum_{i=1}^N \frac{3}{2} \left(\hat{a}_{i,\alpha} \hat{a}_{i,\beta} - \frac{1}{3} \delta_{\alpha\beta} \right), \quad (3)$$

where $\hat{a}_{i,\alpha}$ and $\hat{a}_{i,\beta}$ are the Cartesian components of $\hat{\mathbf{a}}_i$ and $\delta_{\alpha\beta}$ is the Kronecker delta. The nematic order parameter P_2 (for a single snapshot) is associated with the largest-modulus of a non-degenerate eigenvalue of $\mathbf{Q}$ and $\hat{\mathbf{n}}$ is the corresponding eigenvector. In this formulation, zero-energy diffusive motion of $\hat{\mathbf{n}}$ does not have effect on $\langle P_2 \rangle$'s value.

The density modulation is measured by smectic order parameter [73]:

$$\langle \tau \rangle = \frac{1}{\rho} \left\langle \left| \sum_{i=1}^N \exp(i\mathbf{k} \cdot \mathbf{r}_i) \right| \right\rangle, \quad (4)$$

where ρ is number density, $\mathbf{k}$ is a wavevector of density undulation and $\mathbf{r}_i$ are molecules' centers of mass. Typically, for non-tilted smectic phases $\mathbf{k} \parallel \hat{\mathbf{n}}$. For $\langle \tau \rangle = 0$ there is no density modulation, whereas for $\langle \tau \rangle = 1$ the molecules form perfect layers with a spacing equal to $2\pi/|\mathbf{k}|$. In simulations, $\mathbf{k}$ has to be compatible with periodic boundary conditions. It can be achieved by taking a linear combination of reciprocal box vectors with integer coefficients h, k, l (Miller indices) [75]. To find an optimal wavevector, we tested all combinations of $h, k, l \in [-5, 5]$ and selected the ones giving the highest value of τ . Using this method one can avoid assuming $\mathbf{k}$ a priori.

Total polarization can be computed as a sum of molecule polarization vectors

$$\langle \mathbf{M} \rangle = \left\langle \sum_{i=1}^N \hat{\mathbf{b}}_i \right\rangle. \quad (5)$$

As it will be seen from the results, the non-zero polarization can be present when one restricts the summation to a plane perpendicular to $\hat{\mathbf{n}}$, however, at the same time, it can vary in the direction of $\hat{\mathbf{n}}$ and give zero net polarization when summed over the whole system. To account for such variations, one can calculate the norm $M(C_j) = \|\mathbf{M}(C_j \pm \Delta C/2)\|$ for molecules in a narrow shell between two planes $\mathbf{r} \cdot \hat{\mathbf{n}} = C_j \pm \Delta C/2$ and sum them over the whole system:

$$\langle m \rangle = \frac{1}{N_b} \left\langle \sum_{j=1}^{N_b} M(C_j) \right\rangle, \quad (6)$$

where $N_b = L/\Delta C$ is the number of shells and L is the system length in the direction of $\hat{\mathbf{n}}$.

An additional insight into the phase structure can be provided by pair correlation functions [76] (for the $\hat{\mathbf{a}}$ and $\hat{\mathbf{b}}$ vectors, cf. Fig. 2) measured with reference to z -axis:

$$S_{aa}^{220}(R_z) = \left\langle \frac{3}{2} \left(\hat{\mathbf{a}}_i \cdot \hat{\mathbf{a}}_j - \frac{1}{3} \right) \right\rangle_{ij}, \quad (7)$$

$$S_{bb}^{110}(R_z) = \langle \hat{\mathbf{b}}_i \cdot \hat{\mathbf{b}}_j \rangle_{ij}, \quad (8)$$

$$S_{aa}^{221}(R_z) = \langle [(\hat{\mathbf{a}}_i \times \hat{\mathbf{a}}_j) \cdot \hat{\mathbf{z}}_{ij}] (\hat{\mathbf{a}}_i \cdot \hat{\mathbf{a}}_j) \rangle_{ij}. \quad (9)$$

Here, $\langle \dots \rangle_{ij}$ denotes the averaging over all pairs of molecules, whose mass centers' z coordinates differ by $R_z \pm \Delta R_z/2$ (ΔR_z corresponds to numerical bin size) in a single, final snapshot of the system, and $\hat{\mathbf{z}}_{ij}$ is z axis unit vector, pointing from j -th to i -th molecule. $S_{aa}^{220}(R_z)$ parameter measures nematic-like correlations of molecules' main axes $\hat{\mathbf{a}}$. S_{bb}^{110} quantifies the correlation of polarization axes $\hat{\mathbf{b}}$, while S_{aa}^{221} is sensitive to chirality of the structure.

3. Results

3.1. Phase overview

The system exhibits a variety of liquid phases: isotropic liquid (Iso), nematic (N), twist-bend nematic (N_{TB}), non-polar smectic A (SmA), splay-bend smectic (Sm_{SB}) and an unidentified polar smectic (SmX). The phase diagram for hard-core interactions is shown in Fig. 3. WCA soft repulsion recreates all the phases with nearly identical phase borders. All order parameters described by Eq. (2), (4) and (6) are gathered in Fig. 4 as a function of the bend angle χ and the packing fraction η . Finally, system snapshots for all identified phases are depicted in Fig. 5.

For each value of χ and sufficiently low η , the molecules form ordinary isotropic liquid as shown by low values of all order parameters indicating a lack of any long-range correlations (see Fig. 5(a)). Around $\eta = 0.45$ the system crystallizes into several types of hexagonal close-packed crystals, which is beyond the scope of this work. The boundary of the Iso phase moves upwards in η for a decreasing bend angle χ . It can be explained by the fact, that a smaller bend angle results in less prolate molecules, for which the entropic gain from orientational ordering is lower.

3.2. Nematic phases

The ordinary nematic phase N can be observed for $\chi > 110^\circ$, as indicated by a sharp jump of $\langle P_2 \rangle$ value from near zero to over 0.5 on the phase boundary and lack of density modulation (Fig. 5(b)). A growing η results in an increase of $\langle P_2 \rangle$ to almost 0.9 for $\chi \approx 180^\circ$, which is significantly higher than a typical range [0.3, 0.7] for nematics observed in experiments [77]. Additionally, two smallest eigenvalues of $\langle \mathbf{Q} \rangle$ are comparable, which together with a vanishing net polarization $\langle \mathbf{M} \rangle \approx \mathbf{0}$ (result not shown) indicates that the nematic phase is uniaxial. Layer polarization $\langle m \rangle$ is also close to zero, which means that the phase is homogeneous.

The situation changes for a phase forming over the Iso phase for $\chi < 110^\circ$ and over the N phase in the range $\chi \in [110^\circ, 140^\circ]$, for η values between 0.29 and 0.35 (Fig. 5(c)). No density modulation suggests that is a nematic-like phase, however with $\langle P_2 \rangle \in [0.3, 0.5]$, lower than for the ordinary N phase in the system. The net polarization is zero, while $\langle m \rangle$ lies in the range [0.4, 0.8], indicating high polar ordering in planes perpendicular to $\hat{\mathbf{n}}$. A closer inspection (Fig. 6) reveals that this is N_{TB} phase [58,59,49,56]. Assuming the global director is aligned with the z axis (cf. Fig. 1), the director $\hat{\mathbf{n}}$ can be parameterized as

$$\hat{\mathbf{n}}(x, y, z) = \begin{pmatrix} \sin(\theta) \cos(2\pi z/p) \\ \sin(\theta) \sin(2\pi z/p) \\ \cos(\theta) \end{pmatrix}. \quad (10)$$

The spatial dependence of $\mathbf{M}$ is similar, with $\mathbf{M} \perp \hat{\mathbf{n}}$. The pitch and tilt angle vary in phase space – $p \in [25\sigma, 45\sigma]$ and $\theta \in [25^\circ, 35^\circ]$, respectively. With increasing packing fraction η or decreasing bend angle χ the pitch shortens and tilt angle becomes more obtuse. Spatial variations of $\hat{\mathbf{n}}$ and $\mathbf{M}$ fields are reflected by $S_{\alpha\alpha}^{KKL}$ correlation functions plotted in Fig. 6(a) for two sets of parameters: $(\chi, \eta) = (130^\circ, 0.32)$ and $(\chi, \eta) = (100^\circ, 0.33)$. They all have the same period p as the director field. For $\chi = 130^\circ$, S_{aa}^{220} reaches a maximal value 0.8 at $R_z = 0 \equiv p$ indicating a high local nematic order (compared to a global $\langle P_2 \rangle \approx 0.4$ value). In between the maxima, it falls until it reaches the minimal value of -0.3 for $R_z = p/2$ when local preferred directions of long molecular axes have an opposite tilt. The S_{bb}^{110} function follows a sinusoidal pattern, which can be predicted assuming the polarization field rotates in the xy plane. Notice that the amplitude is lower than 1, namely, S_{bb}^{110} reaches ± 0.5 . It

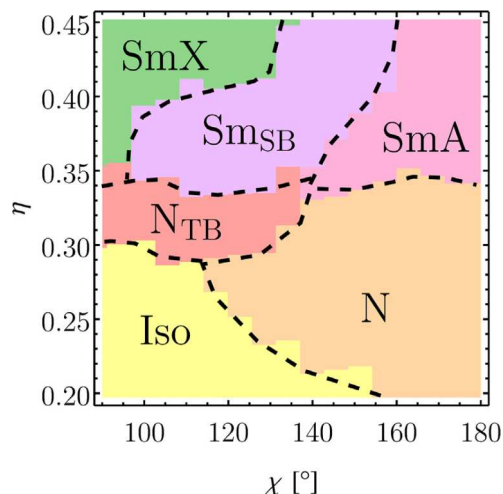


Fig. 3. Phase diagram for hard-core interactions in (χ, η) parameters space. The following phases are present: isotropic liquid (Iso), nematic (N), twist-bend nematic (N_{TB}), non-polar smectic A (SmA), splay-bend smectic (Sm_{SB}) and unidentified polar smectic (SmX). Black dashed lines are arbitrarily drawn to visually separate the phases' regimes. For $\chi \in [90^\circ, 180^\circ]$ and $\eta < 0.35$ the phase sequences are in line with the results from the mean-field theory [37,27].

suggests, that vectors $\hat{\mathbf{b}}$ have a local spread. A non-zero value of S_{aa}^{221} confirms that the director field is chiral. For a smaller bend angle, i.e. $\chi = 100^\circ$, all correlation functions are qualitatively identical, however, one can see some quantitative differences. S_{aa}^{221} parameter remains unchanged. S_{aa}^{220} has a comparable maximal value meaning that a local nematic order is similar, however, the minimum is broader and of a higher magnitude, which is expected for a wider tilt angle θ . At the same time, the amplitude of S_{bb}^{110} increases to 0.7 suggesting a lower local spread of molecules' polarization vectors. It is confirmed by a higher value of $\langle m \rangle$ for $\chi = 100^\circ$ bend angle compared to $\chi = 130^\circ$.

N_{TB} can be described using phenomenological lowest-order² Oseen-Zocher-Frank elastic free energy density [78–80]

$$F_{OZF} = \frac{1}{2} K_{11} [\hat{\mathbf{n}}(\nabla \cdot \hat{\mathbf{n}})]^2 + \frac{1}{2} K_{22} [\hat{\mathbf{n}} \cdot (\nabla \times \hat{\mathbf{n}})]^2 + \frac{1}{2} K_{33} [\hat{\mathbf{n}} \times (\nabla \times \hat{\mathbf{n}})]^2, \quad (11)$$

where subsequent terms represent, respectively, splay, twist, and bend deformations of director field and K_{ii} ($i = 1, 2, 3$) are Frank elastic constants. All three Frank elastic constants have to obey Ericksen's inequalities [81], i.e.: $K_{ii} \geq 0$ ($i = 1, 2, 3$), otherwise perfect alignment (homogeneous nematic) would not correspond to a state of minimum energy. However, if one were to consider a scenario where $K_{33} < 0$, then it would occur that bend deformation is energetically favorable and the reference state, namely a homogeneous nematic, becomes unstable [19]. As there does not exist a (two-dimensional) structure with constant bend without topological defects, it has to be combined with at least one of the other deformations, either splay or twist. If $K_{11}/K_{22} > 2$, then the frustration is diminished through escape into third dimension, which leads to the stabilization of twist-bend structure, whereas for $K_{11}/K_{22} < 2$ two dimensional splay-bend structure emerges [19]. As pointed out by Shamid *et al.* [59], the effective K_{33} constant can become negative below a certain critical temperature, when

² This is a valid approach that provides qualitative results but in order to reflect experimental data a more holistic method should be incorporated [28].

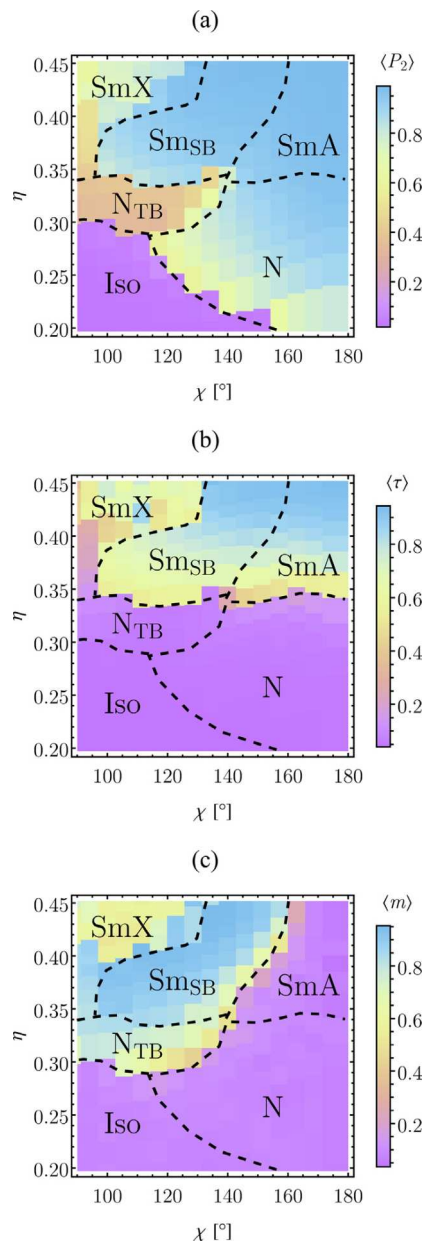


Fig. 4. Ensemble averages of order parameters as a function of χ and η . (a) Nematic order parameter $\langle P_2 \rangle$, (b) smectic order parameter $\langle \tau \rangle$ and (c) layer polarization $\langle m \rangle$.

the coupling of polarization with bend deformation is introduced, supporting the assumption that N_{TB} is inherently polar. The phase can be also understood through geometrical reasoning [37,82,27,28]. For curved spherocylinders, one can predict a correct relation between molecule bend angle, pitch p , and tilt angle θ matching the spherocylinder curvature with an integral curve of a director field $\hat{n}$ [56].

3.3. Smectic phases

For $\eta > 0.34$, smectic phases are formed. The N phase is adjacent to an ordinary SmA phase – $\langle \tau \rangle$ is over 0.5 and strata are clearly visible [Fig. 5(d)]. Further compression narrows the spread

of molecules' mass centers in the direction normal to the layer and τ approaches unity for a high η . Typically, $\langle P_2 \rangle$ value experiences a jump on the N-SmA boundary from around 0.4–0.6 to over 0.8 [58], however in some systems it is small or absent [52]. Here, no abrupt change of $\langle P_2 \rangle$ is observed. Molecule polarizations are chaotic within the layers, as indicated by a low value of $\langle m \rangle$ and they are orthogonal to $\hat{n}$.

A distinct smectic phase is formed over N_{TB} phase for $\chi > 100^\circ$ and over SmA for $\chi \in [140^\circ, 160^\circ]$ [see Fig. 5(e)]. A high value of $\langle m \rangle$ indicates that it is a polar phase and a closer inspection shows that adjacent layers have an opposite (antiferroelectric) polarization. Further analysis reveals that the director $\hat{n}(x, y, z)$ varies in space. The numerical data is well described by a director field

$$\hat{n}(x, y, z) = \begin{pmatrix} \frac{\sin(\theta) \cos(2\pi z/p)}{0} \\ \sqrt{1 - \sin^2(\theta) \cos^2(2\pi z/p)} \end{pmatrix}, \quad (12)$$

thus the phase was identified as splay-bend smectic (Sm_{SB}). The director is constant in xy plane and oscillates within xz plane around $\hat{z}$ direction, coinciding with the direction $\mathbf{k}$ of density modulation. It is, however, important to note that Sm_{SB} phase emerging in our model is slightly different from the one observed in Ref. [56]. There, the density modulation is non-zero within a whole period and molecules are present between the density maxima [see Fig. 10(a) from Ref. [83]]. On the other hand, in our system, the density is non-zero only near the layer's middle [see Fig. 5(e)] with almost no molecules between the layers. Nonetheless, Eq. (12) holds in the area of non-zero molecule density, thus regarding the phase as Sm_{SB} emphasizes the presence of the director field's modulation.

Although $\hat{n}(x, y, z)$ leans from $\mathbf{k}$ for a fixed z value, averaging over the whole layer gives $\hat{n} = 1/p \int_0^p \hat{n}(x, y, z) dz$ which is parallel to $\mathbf{k}$. Consequently, if one disregards the spatial dependence of the director field and the classification is performed solely on the layer-averaged director and polarization, the phase can be identified as antipolar smectic A (Sm_{AP_A}) [38,84], observed for V-like shaped hard-core molecules in Ref. [52].

The onset of polar order may be attributed to the entropic gain of translational motion within a layer, however, it does not explain the antiferroelectric arrangement of layer polarization. Lansac *et al.* [52] ascribed such configuration to the more compatible vibrational motion of two molecules from adjacent layers when they have antiparallel directions compared to parallel ones, resulting in once again in a higher entropy of the former system. Sm_{SB} -SmA boundary moves to higher densities for less bent molecules – lower curvatures discourage polar order, so a stronger compression is required to achieve it. In particular, for $\chi > 160^\circ$, a crystallization occurs before the formation of Sm_{SB} ³. Note that N_{TB} always forms (locally) polar smectic when compressed, which is to be expected since N_{TB} is already (locally) polar.

The director fields (10), (12) are special cases of a more general one [56]:

$$\hat{n}(x, y, z) = \begin{pmatrix} \frac{\sin(\theta_a) \cos(2\pi z/p)}{\sin(\theta_b) \sin(2\pi z/p)} \\ \sqrt{1 - \sin^2(\theta_a) \cos^2(2\pi z/p) - \sin^2(\theta_b) \sin^2(2\pi z/p)} \end{pmatrix}, \quad (13)$$

where the angles θ_a and θ_b may be different. Fixing $\theta_a = \theta$ and continuously changing θ_b from 0 to θ interpolates between director fields for N_{TB} and Sm_{SB} . This intermediate splay-twist-bend smectic (Sm_{STB}) phase has been observed, at present, exclusively for bent spherocylinders [56]. In our model, however, it is absent. One of

³ Notably, the crystal is polar for $\chi \in [160^\circ, 170^\circ]$ and non-polar above $\chi = 170^\circ$.

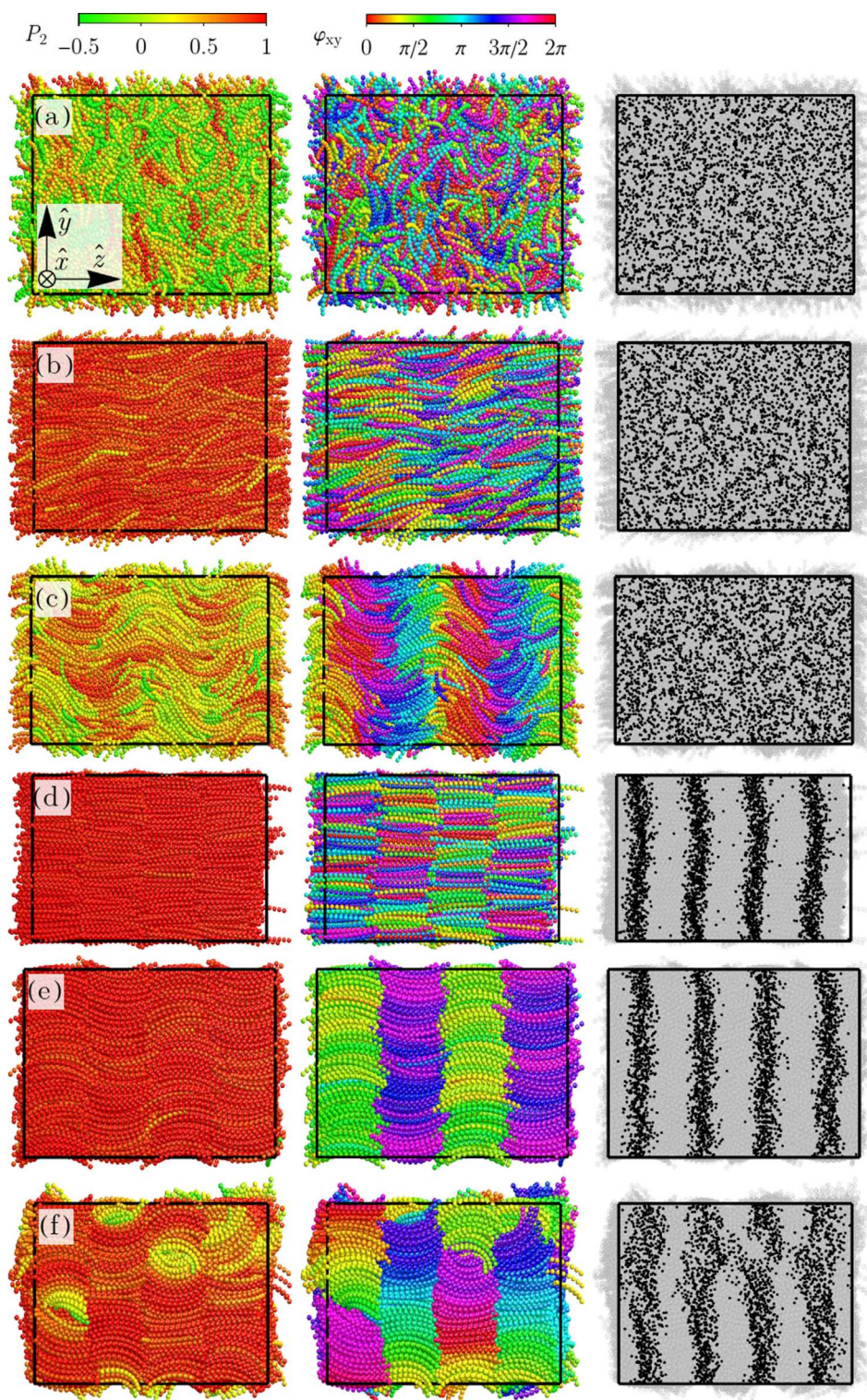


Fig. 5. System snapshots for all identified phases. Each row represents one phase: (a) Iso [$(\chi, \eta) = (95^\circ, 0.27)$], (b) N [$(\chi, \eta) = (140^\circ, 0.31)$], (c) N_{TB} [$(\chi, \eta) = (100^\circ, 0.32)$], (d) SmA [$(\chi, \eta) = (160^\circ, 0.39)$], (e) Sm_{SB} [$(\chi, \eta) = (130^\circ, 0.39)$], (f) SmX [$(\chi, \eta) = (100^\circ, 0.41)$]. In the first column molecules are color-coded according to P_2 value, in the second one – according to molecule polarization angle φ_{xy} between x axis and the projection of $\mathbf{b}$ onto xy plane. Finally, in the last column, black dots represent molecules' mass centers.

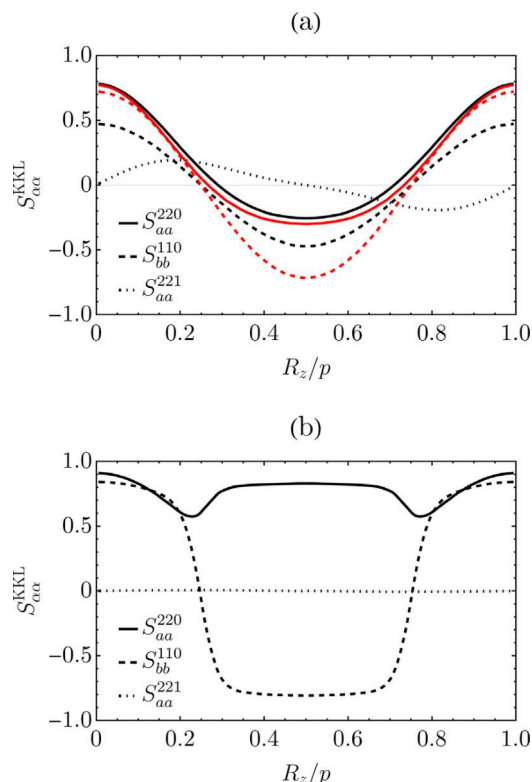


Fig. 6. Pair correlation functions $S_{\alpha\alpha}^{KKL}$ for (a) N_{TB} phase $[(\chi, \eta) = (130^\circ, 0.32)]$ – black lines and $(\chi, \eta) = (100^\circ, 0.33)$ – red lines] and (b) Sm_{SB} phase $[(\chi, \eta) = (115^\circ, 0.37)]$. Solid, dashed and dotted lines correspond to, respectively, S_{aa}^{220} , S_{bb}^{110} and S_{aa}^{221} . S_{aa}^{221} parameter for $(\chi, \eta) = (100^\circ, 0.33)$ is not shown, since it overlaps with the one for $(\chi, \eta) = (130^\circ, 0.32)$. The distance R_z is given in units of the structure's period (for Sm_{SB} it is a width of two layers).

the reasons might be the length of the molecules (ours are shorter than in Ref. [56]) or undulated surface created by beads (contrary to a smooth one in Ref. [56]), which hinders sliding of the molecules along themselves.

Correlation functions for $(\chi, \eta) = (115^\circ, 0.37)$ are shown in Fig. 6(b). Here, due to the antiferroelectric arrangement, the period p is the width of two layers. Nematic-like correlations measured by S_{aa}^{220} are high in a whole range with two shallow minima around $R_z = p/4$ and $R_z = 3p/4$. These R_z values are the distances between a middle of a layer and a space between layers, where molecules are very scarce and less ordered, which as a result lowers S_{aa}^{220} . A lower value for $R_z = p/2$ when compared to $R_z = 0, p$ may be attributed to splay-bend modulation of the director field (12) – although

the directors in the middle of adjacent, antipolar layers are parallel, away from the middle, the director tilts in a different direction. S_{bb}^{110} reaches 0.8 for $R_z \in [0, 0.2p]$ and $R_z \in [0.8p, p]$, representing the high correlations of polarization within the layer and two layers further, respectively, while for $R_z \in [0.3p, 0.7p]$, S_{bb}^{110} is equal to -0.8 confirming anti-correlations in adjacent layers. Since the structure is achiral, S_{aa}^{221} is zero in the whole range of R_z .

Highly bent molecules form yet another polar smectic phase, as indicated by high $\langle \tau \rangle$ and $\langle m \rangle$ values, however of an unknown type, thus denoted as SmX [see Fig. 5(f)]. Despite trying both compression and expansion from various initial configurations (dense crystal, diluted crystal, type C smectic, lower-density equilibrium system, and others), as well as relaxation in a triclinic simulation box, where both the side lengths and the angles between the box faces are allowed to change, we were not able to obtain a structure without irregular domain walls. As it can be seen from Fig. 5, the polarization within each stratus rotates with y coordinate and topological defects are visible. The same effects are present for both hard and soft interactions. Increasing the system size, which allows a full rotation of the molecule polarization vector has not eliminated the defects and in neither case they form a regular pattern as in, e.g., blue phases [85]. However, the blue-phase-like structures cannot be completely disregarded since the lattice constant of the defects can be of the order of tens or even hundreds of molecule lengths, and the system size allowing such long periods is far beyond the limit of our computational resources. Another candidate is antclinic, antiferroelectric type C smectic ($SmC_A P_A$) [38,84]. There, both the director tilt and polarization alternate between layers. Remarkably, we have observed its formation for a very acute bend angle $\chi < 70^\circ$ and a high density $\eta > 0.4$ (see Fig. 7).

BSMs with highly acute bend angles are still scarce and not fully understood [84,86]. Chemical data indicate that increasing the mesogens' degree of bend decreases the LC phase stability, which leads to a loss of mesogenic properties [87]. Therefore, $\chi < 90^\circ$ falls outside of the scope of this work. Nevertheless, further investigation of the unidentified SmX phase can be a potential goal for future studies.

Our simulation results correlate well with the experimentally observed phase sequences for BSMs [88,16,89]. Additionally, the mapped region of N_{TB} 's stability, governed by the bend angle, is in fairly good agreement with the empirical data [90,17,91].

The studied system undergoes following phase transitions:

- Iso $\leftrightarrow$ N $\leftrightarrow$ SmA,
- Iso $\leftrightarrow$ N $\leftrightarrow$ SmA $\leftrightarrow$ Sm_{SB},
- Iso $\leftrightarrow$ N $\leftrightarrow$ N_{TB} $\leftrightarrow$ Sm_{SB},
- Iso $\leftrightarrow$ N $\leftrightarrow$ N_{TB} $\leftrightarrow$ Sm_{SB} $\leftrightarrow$ SmX,
- Iso $\leftrightarrow$ N_{TB} $\leftrightarrow$ Sm_{SB} $\leftrightarrow$ SmX,
- Iso $\leftrightarrow$ N_{TB} $\leftrightarrow$ SmX.

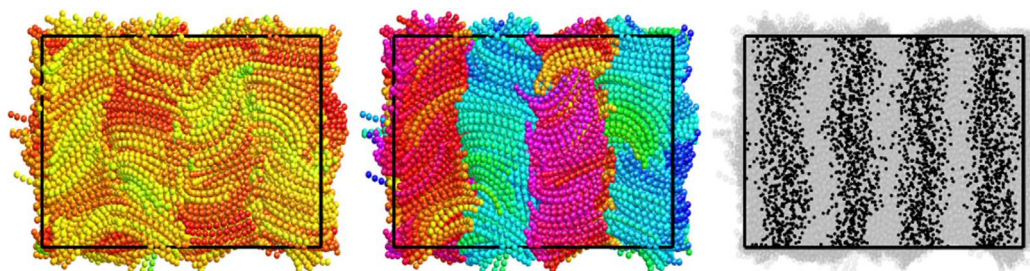


Fig. 7. System snapshot for $SmC_A P_A$ phase $[(\chi, \eta) = (65^\circ, 0.45)]$ in analogy to Fig. 5.

Sequence (a) is quite common in systems composed of BSMs [89] in contrary to sequences (b-f). As far as we know, in the literature are reported only variants of twist-bend smectic phase [92,93] without any mentions of splay-bend smectic. What is more, the compounds that form N_{TB} directly from Iso are uncommon [88]. On the other hand, there are some premises that SmX might be one of smectic phases outlined in [94,95]. For the CB6O. Sm series ($m = 13, 15, 17$) following phase sequence was found [96]: $Iso \leftrightarrow N \leftrightarrow SmA \leftrightarrow SmX \leftrightarrow SmC_{TB}$, which is similar to sequence (b).

At this point, it is worth emphasizing the fact that the twist-bend nematic phase was identified exclusively in thermotropic systems, whereas the splay-bend nematic (N_{SB}) solely in colloidal systems of “banana-shaped” particles [23] and bent silica rods [97]. The discovery of thermotropic N_{SB} and N_B , along with lyotropic N_{TB} [98], will constitute the next key milestones on the roadmap of liquid crystal science.

4. Conclusions

We have systematically studied the phase diagram of the liquids formed by bent-shaped molecules composed of tangential spheres with centers placed on an arc. The molecules were described by adjustable bend angle χ and the system composed of such molecules was considered under different packing fractions η . In (χ, η) parameters space, we have identified following phases: isotropic, nematic, twist-bend nematic, smectic A, and splay-bend smectic. For the highest density and the largest χ we have observed a smectic phase, denoted as SmX, forming polar layers with in-layer rotating polarization. We were, however, not able to avoid defects and domain walls. For unrealistically large bend, SmX phase transformed to anticlinic, antiferroelectric type C smectic, where both the director tilt and polarization alternate between layers. In comparison to a previous study for bent spherocylinders [56], we have not observed splay-twist-bend smectic. The obtained results were the same for both: MC with hard-core interactions and MD using short-range WCA repulsion.

Data availability

The datasets generated during and/or analyzed during the current study are available from P.K. and W.T. upon reasonable request.

Code availability

The source code of an original simulation package used to perform Monte Carlo sampling is available at <https://github.com/PKua007/rampack>. Input script for LAMMPS is available from W. T. upon reasonable request.

Author Contributions

P.K.: conceptualization, data curation, formal analysis, funding acquisition, investigation, project administration, software, visualization, writing. W.T.: conceptualization, data curation, formal analysis, investigation, validation, visualization, writing. M.C.: conceptualization, writing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Relationship between the size of bent-shaped molecules and mesophase formation: a computational study

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Abstract

Mesogenic properties stem from the right conditions imposed by the molecular structure of molecules. Knowledge of how, for example, alterations in molecules' length-to-width ratio affect the mesophase emergence is of key importance and paves pathways for new discoveries. Motivated by the ongoing research revolving around the nature of twist-bend nematic phase and its structural traits, we conducted Monte Carlo simulations of bent-shaped molecules represented as a rigid set of hard, tangent spheres evenly attached along the arc. With a fixed bend angle and a variable number of spheres (n), we have examined the relative stability of the twist-bend nematic phase and constructed the phase diagram in the domain of n and packing fraction η . Subsequent phases were identified: isotropic, nematic, twist-bend nematic, smectic A, splay-bend nematic, crystal, and type 1 columnar banana phase – for the first time being reported in a computational study.

Keywords: Liquid crystals, Bent-shaped molecules, Twist-bend nematic, Banana phases, Mirror symmetry breaking, Monte Carlo simulations

1. Introduction

Liquid crystals (LCs) constitute a remarkable intermediate state of matter in between the liquid and the crystal, possessing the properties of both [1]. The simplest among a variety of different liquid crystalline phases is the nematic (N). This mesophase is a result of the self-assembly of anisotropic molecules, which tend – on average – to align along the preferred direction, termed as a “director” ($\hat{n}$). Additionally, the molecules' centers of mass are distributed randomly over the sample volume. Preserving the latter feature (to some extent) and simultaneously inducing periodicity in $\hat{n}$ by adding position dependence leads to a broad family of nematic modulated structures of assorted complexity [2–4]. For example, in chiral nematic, the director field forms a helix, whereas in blue phases, the director field with a double twist is comprised of tubes stacked upon one another to generate cubic lattices stabilized by disclinations (linear defects). Over the years, a variety of modulated structures have been predicted theoretically (see e.g. [5–14]) and several of which have been confirmed experimentally [15–20] – one of them is twist-bend nematic (N_{TB}).

A remarkable hallmark of N_{TB} (Fig. 1) is that this chiral phase is formed in systems composed of achiral mesogens and constitutes the first example of spontaneous mirror symmetry breaking (SMSB) in a liquid state with no support from long-range spatial ordering [21]. This has far-reaching implications

that manifest in the form of a heliconical (modulated in one dimension only) structure of a nanoscale pitch with a ground state characterized by a degenerate sign of chirality (so-called “ambidextrous chirality”) resulting in a co-existence of helices with both handednesses: left and right. Peculiar also is the behavior and hierarchy of elastic constants in a nematic phase (see e.g. [22, 23]), that precedes¹ N_{TB} upon cooling from an isotropic phase. In no time, N_{TB} became a prominent subject of attention within the community of liquid crystalline researchers around the world [25].

Nowadays an immense amount of compounds is known to exhibit the N_{TB} phase, i.a.: dimers [15–17, 26–30], trimers, tetramers, and higher oligomers [31, 32], along with hybrid bent-core LC [33] and hydrogen bonded oligomers [34]. Additionally, some N_{TB} -forming mixtures were reported [27, 35]. All that owes to the Meyer's [6] and Dozov's [7] conjecture supported by computer simulations [14, 36–38], that the properly “curved” (bent) shape of the molecules is sufficient to stabilize the N_{TB} . Nevertheless, some aspects of the molecules' structure still merit insightful examination. One of them is how the molecules' size affects the stability of N_{TB} . In that context, very famous are CB_nCB (the 1, ω -bis(4-cyanobiphenyl-4'-yl) alkane homologous series; for chemical structure see Fig. 2b) dimers, where solely the odd members form N_{TB} .

Generally, several phenomena are related to the mesomorphic homologous series, e.g.: the existence of an odd–even effect [39], (de)stabilization of mesomorphic properties [40, 41] and the tendency to form either nematic or smectic phases [40–

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¹Mesogens that form N_{TB} directly from isotropic phase are known in the literature [24].

42]. What is more, for dimers, one can also observe appearance of interdigitated and intercalated smectic phases or some counter-intuitive behaviors like the promotion of nematic phase upon an increment of molecules' length [43].

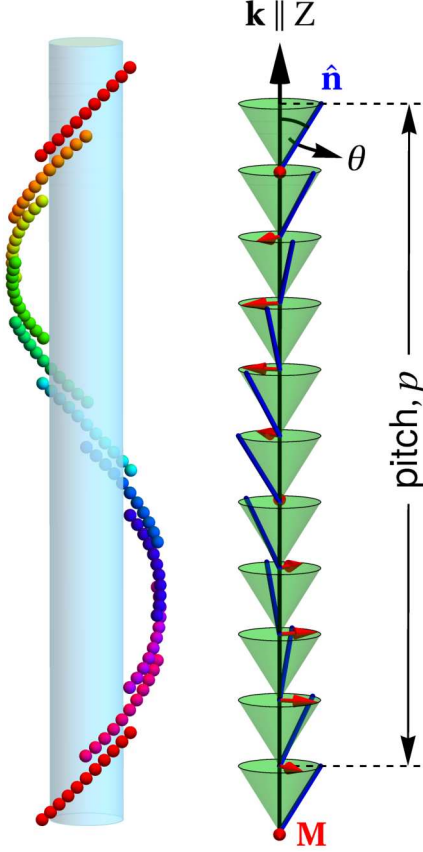


Figure 1: Helical arrangement (one of the two degenerate domains) of achiral, bent-shaped molecules in twist-bend nematic phase. Key aspects of N_{TB} comprise: finite pitch p (usually a few nanometers); tilt angle θ ($0 < \theta < \pi/2$) between the director $\hat{n}$ and helical axis $\mathbf{k} \parallel Z$ ($\mathbf{k} = k\hat{z} = (2\pi/p)\hat{z}$); the polarization $\mathbf{M}$ ($\mathbf{M} \parallel \hat{n} \times \mathbf{k}$) is precessing around $\mathbf{k}$ along with $\hat{n}$; lack of density modulation.

2. Model systems and computational methods

2.1. Molecular model

Here, we delve into the investigation of stability-structure dependence, initiated in Ref. [38], by varying the length of the molecules with a determined curvature through either adding or subtracting subsequent spheres. As our reference state, we choose a molecule composed of eleven tangent spheres of diameter σ placed on a circular arc. The measure of the arc's curvature, designated onward as molecule's bend angle χ , is defined as the angle formed by two lines, tangent to the arc at the centers of end-point spheres (see Fig.2c). We set $\chi = 130^\circ$ as it has been shown that mesogens with such bend angle tend to form the twist-bend nematic phase [37, 38, 44–47].

Entropy driven formation of liquid crystalline phases has been extensively studied for rigid bodies [48]. Thus we focus on a hard-sphere model, where the interaction energy is zero if the constituent spheres are disjoint, while for overlapping spheres, the energy is infinite [49]. Consequently, for a fixed angle χ , the only two independent parameters are the number of spheres n and the packing fraction η .

2.2. Computer simulations

We performed constant pressure (NPT) Monte Carlo (MC) simulations for all n between 7 and 15 (Fig. 2a), with $N = 7200$ for $n \in [7, 9]$ and $N = 4800$ for $n \in [10, 15]$ in a box with periodic boundary conditions (PBC). To scan various packing fractions between $\eta \approx 0.2$ and $\eta \approx 0.5$, each system was simulated under various pressures from the range $P \in [1, 10]$. The initial configurations were slightly diluted antiferroelectric hexagonal crystals with $\eta \approx 0.42$, with 6 layers for $n \in [7, 9]$ and 4 layers for $n \in [10, 15]$. More precisely, in a single layer, mass centers' were arranged in a hexagonal honeycomb pattern and molecules' orientations were identical, with $\hat{\mathbf{a}}$ perpendicular and $\hat{\mathbf{b}}$ parallel to the layer; adjacent layers were identical, except the opposite sign of the polarization axes $\hat{\mathbf{b}} \leftrightarrow -\hat{\mathbf{b}}$. The initial configuration was then thermalized for 10^8 MC cycles under pressure $P = 8 - 10$ to retain the original $\eta \approx 0.42$ packing density. Such equilibrium systems were then used as the starting point for the rest of simulations – the system was compressed or expanded to all target pressures in parallel. Because of model molecule's concavities, the equilibration was slow, requiring from 5×10^7 to 5×10^8 MC cycles. The production (averaging) phase lasted for at least 5×10^7 cycles.

Each MC cycle consisted of N molecular rototranslation moves and a single box move. The molecular move consisted of selecting a molecule at random, translating it by a random vector and rotating it around a random axis by a random angle. If the move did not introduce an overlap, it was accepted; otherwise, it was rejected. Box move was made by performing an appropriate box deformation and accepting it according to the Metropolis-Wood criterion [50]. Smectic phases were simulated in a general triclinic box in which all components of box vectors were perturbed, while nematic and isotropic phases were simulated in an orthorhombic box, where only the side lengths were altered.

2.3. Order parameters and correlation functions

For the purpose of quantification and description of observed phases, we have employed a set of order parameters and correlation functions. Nematic order can be quantified using the second-rank order parameter [1]:

$$P_2 = \frac{1}{N} \sum_{i=1}^N P_2(\hat{\mathbf{a}}_i \cdot \hat{\mathbf{n}}), \quad (1)$$

where the sum is over all N molecules in the system, $P_2(\dots)$ is the Legendre polynomial of degree 2 and $\hat{\mathbf{a}}_i$ is a molecular axis vector of i -th molecule (cf. Fig. 2c).

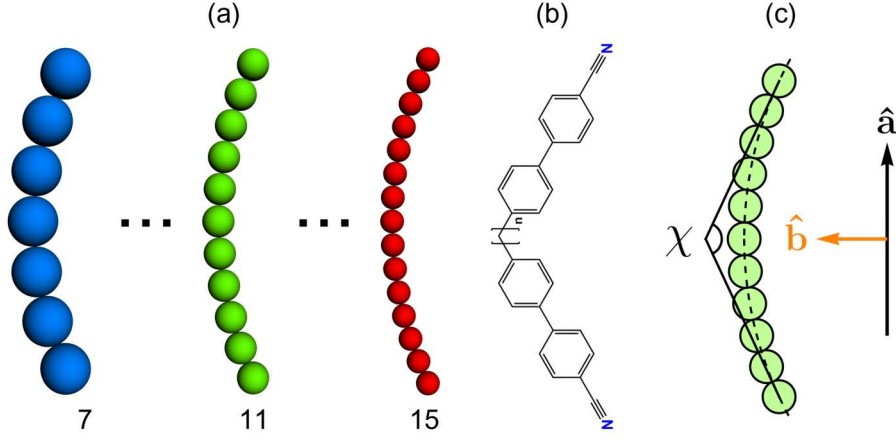


Figure 2: (a) Tangent n spheres, where $n \in [7, 15]$, with fixed curvature being defined in (c). (b) Chemical structure of CB_nCB homologs series where “CB” stands for “cyanobiphenyl” and “ n ” the number of methylene units in the spacer. (c) Schematic representation of our tangent hard-sphere molecule model with $n = 11$; χ denotes the bend angle, $\hat{\mathbf{a}}$ is the long molecular axis, and $\hat{\mathbf{b}}$ is the short molecular axis (parallel to polarization axis).

In general, if the director $\hat{\mathbf{n}}$ is not assumed *a priori*, the instantaneous value of P_2 for a single snapshot can be computed using the $\mathbf{Q}$ -tensor [1]:

$$\mathbf{Q} = \frac{1}{N} \sum_{i=1}^N \frac{3}{2} \left(\hat{\mathbf{a}}_i \otimes \hat{\mathbf{a}}_i - \frac{1}{3} \right), \quad (2)$$

where the sum goes over all molecules in the system. Then, P_2 is computed as $\mathbf{Q}$ -tensor’s non-degenerate eigenvalue with the largest-modulus and the corresponding eigenvector is the director $\hat{\mathbf{n}}$. Finally, it is averaged over many system snapshots for better statistics (ensemble averaged value will be denoted as $\langle P_2 \rangle$). For an ideal nematic, where all long molecular axes ($\hat{\mathbf{a}}$) are parallel, $\langle P_2 \rangle = 1$, while for an isotropic liquid: $\langle P_2 \rangle = 0$.

Layer formation may be probed using the smectic order parameter [1]:

$$\langle \tau \rangle = \left\langle \frac{1}{N} \left| \sum_{i=1}^N \exp(i\mathbf{k} \cdot \mathbf{r}_i) \right| \right\rangle, \quad (3)$$

where $\langle \dots \rangle$ denotes ensemble averaging, i is the imaginary unit, $\mathbf{k}$ is wavevector and $\mathbf{r}_i$ is the position of i^{th} molecule’s mass center. Please note that the modulus $|\dots|$ is taken before ensemble averaging to accommodate for a diffusive drift of smectic order parameter’s complex phase. For a disordered system $\langle \tau \rangle = 0$, while for perfectly layered one $\langle \tau \rangle = 1$. The wavevector $\mathbf{k}$ must be compatible with the periodic boundary conditions; thus, its possible values may be enumerated using Miller indices [51]:

$$\mathbf{k}_{hkl} = h\mathbf{g}_1 + k\mathbf{g}_2 + l\mathbf{g}_3, \quad (4)$$

where $\mathbf{g}_i$ are reciprocal box vectors. One should select hkl indices giving the highest $\langle \tau \rangle$ value. As the systems are initially prepared in a layered configuration, we fix hkl at 004 or 006, depending on the number of layers.

The tendency to form a hexagonal honeycomb structure within the layers may be detected using local hexatic bond or-

der parameter. In 2D, it is defined as

$$\langle \psi_6 \rangle = \left\langle \frac{1}{N} \sum_{i=1}^N \frac{1}{6} \left| \sum_{j=1}^6 \exp(6i\theta_{ij}) \right| \right\rangle. \quad (5)$$

The inner summation goes over six nearest neighbors of i^{th} molecule and θ_{ij} is the angle between the vector joining i^{th} and j^{th} molecule and an arbitrary direction. It should be noted that the hexatic bond order parameter is usually defined globally, with the modulus enclosing both sums. Then, it can detect long-range bond order in phases such as type B or I smectic [1], where local bonds retain the same direction throughout the whole system. We, however, focus on local ordering only, which is reflected in Eq. (5). To generalize the definition to three dimensions, we project molecules’ mass centers onto the nearest layer plane and proceed with the 2D formula. The maximum value of $\langle \psi_6 \rangle$ is 1 for a perfect hexagonal honeycomb structure, while for a disordered smectic $\langle \psi_6 \rangle \approx 0.37$. In order to extend the procedure to non-layered phases, the simulation box is artificially partitioned into four or six layers (in consonance with $\mathbf{k}_{hkl}$).

It is also important to quantify both local and global ordering of molecules’ polarization axes $\hat{\mathbf{b}}$. As the results will show, polarization vector, otherwise constant in a plane, may change when moving in the orthogonal direction (wavevector $\mathbf{k}$). Thus, we measure the planar polarization as

$$\langle M \rangle = \left\langle \frac{1}{N} \sum_{l=1}^{n_L} \left\| \sum_{i \in \text{layer } l} \hat{\mathbf{b}}_i \right\| \right\rangle. \quad (6)$$

The system is divided into n_L layers. It should be as high as possible (for $N \rightarrow \infty$ and $n_L \rightarrow 0$ the sum changes into the integral along the wavevector), as long as the number of molecules within the layer is large enough to preserve good statistics. We chose $n_L = 50$ as a compromise. The outer sum $\sum_{l=1}^{n_L} \dots$ goes over all n_L layers, while the inner sum $\sum_{i \in \text{layer } l} \dots$ iterates all

molecules withing the l^{th} layer and $\|\cdot\|$ is the standard L^2 norm of a vector. The polarization $\langle P \rangle$ reaches 1 in a maximally polarized system and vanishes in a non-polar one.

To compute local polarization, we define

$$\langle m^{(r)} \rangle = \left\langle \frac{1}{N} \sum_{i=1}^N \frac{1}{r+1} \left\| \sum_{j \in r\text{NN}, i} \hat{\mathbf{b}}_j \right\| \right\rangle, \quad (7)$$

where the inner sum goes over the set with i^{th} particle and its r nearest neighbors. We found that $r = 9$ gives a good compromise between statistics and locality, and we will write $\langle m^{(9)} \rangle \equiv \langle m \rangle$. Local polarization $\langle m \rangle$ reaches 1 for a maximally polarized system and, for $r = 9$, falls to $\langle m \rangle \approx 0.36$ in a non-polar system.

Further insight into the observed mesostructures can be given by a carefully selected set of pair correlation functions. The S -expansion functions [52] were proved to be a robust indicator of director and polarization fields' modulations [38]. We will use the following three correlation functions to measure the variation in the direction of system's wavevector [52]:

$$S_{aa}^{220}(\Delta z) = \left\langle \frac{3}{2} (\hat{\mathbf{a}}_i \cdot \hat{\mathbf{a}}_j)^2 - \frac{1}{2} \right\rangle_{ij}, \quad (8)$$

$$S_{bb}^{110}(\Delta z) = \langle \hat{\mathbf{b}}_i \cdot \hat{\mathbf{b}}_j \rangle_{ij}, \quad (9)$$

$$S_{aa}^{221}(\Delta z) = \left\langle [(\hat{\mathbf{a}}_i \times \hat{\mathbf{a}}_j) \cdot \hat{\mathbf{z}}_{ij}] (\hat{\mathbf{a}}_i \cdot \hat{\mathbf{a}}_j) \right\rangle_{ij}, \quad (10)$$

where $\hat{\mathbf{a}}_i$ and $\hat{\mathbf{b}}_i$ are, respectively long molecular and polarization axes of molecule i , $\langle \cdots \rangle_{ij}$ is averaging over all pair of molecules with their z coordinates differing by around Δz and $\hat{\mathbf{z}}_{ij}$ is the z -axis versor pointing from molecule j to molecule i . The first function $S_{aa}^{220}(\Delta z)$ measures nematic-like correlation, the second one $S_{bb}^{110}(\Delta z)$ quantifies polar correlations, while the last one $S_{aa}^{221}(\Delta z)$ indicates whether there is chirality in the system.

3. Results

Within the analyzed molecular model following phases were observed²: isotropic (Iso), nematic (N), twist-bend nematic (N_{TB}), smectic A (SmA), splay-bend smectic (Sm_{SB}) and type 1 banana phase (B_1). The phase diagram in (n, η) parameters is shown in Fig. 3, while system snapshots are gathered in Fig. 4 (nematic phases), and Fig. 5 (smectic phases). Finally, order parameters as a function of (n, η) are plotted in Fig. 6.

The nematic phase is present for all studied values of n , however, the Iso-N phase boundary rises quickly with decreasing n – from $\eta = 0.19$ for $n = 15$ to $\eta = 0.35$ for $n = 7$ (Fig. 3a). In the whole range, all order parameters, except $\langle P_2 \rangle$ have low values (Fig. 6). On the other hand $\langle P_2 \rangle$ is high, in the range between $[0.5, 0.8]$, which is similar to other computational studies of hard-core shapes [38, 53–55]. It should be noted, however,

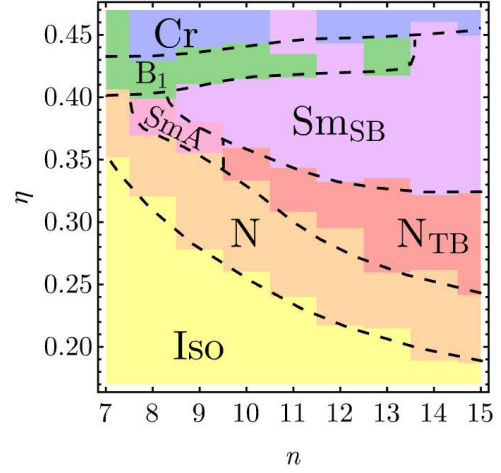


Figure 3: Phase diagram as a function of spheres' number n and packing fraction η . The following phases are present: isotropic (Iso), nematic (N), twist-bend nematic (N_{TB}), type A smectic (SmA), splay-bend smectic (Sm_{SB}), type 1 banana phase (B_1). Around $\eta \approx 0.44$, the system crystallizes; crystalline structure identification is beyond the scope of this manuscript.

that in experiments $\langle P_2 \rangle$ is usually slightly lower, i.e. between 0.4 and 0.7 [56]. The value of $\langle P_2 \rangle$ is approximately constant on both lower and upper nematic phase boundaries and increases with packing fraction η . We also observe a slight increase of local polarization $\langle m \rangle$ near the upper boundary from the disorder value $\langle m \rangle \approx 0.36$ to $\langle m \rangle \approx 0.45$, which is expected, since the N_{TB} phase is locally polar (as will be discussed upon in the next paragraph). The range of the nematic phase in packing fraction is near constant with $\Delta\eta \approx 0.05$.

The acclaimed theory by Oseen-Zocher-Frank (OZF) [57–59] describes spatial distortions of a uniform director field $\hat{\mathbf{n}}$ in a nematic liquid crystal. The resulting elastic free energy density, invariant under rotations and complying with the phase symmetry, is given by following positive-definite quadratic form in the spatial gradients $\nabla \hat{\mathbf{n}}$:

$$2\mathcal{F}_{\text{OZF}} = K_{11}[\hat{\mathbf{n}}(\nabla \cdot \hat{\mathbf{n}})]^2 + K_{22}[\hat{\mathbf{n}} \cdot (\nabla \times \hat{\mathbf{n}})]^2 + K_{33}[\hat{\mathbf{n}} \times (\nabla \times \hat{\mathbf{n}})]^2, \quad (11)$$

where K_{ii} ($i = 1, 2, 3$) are Frank's elastic constants³ corresponding to splay, twist, and bend distortions, respectively, and are material moduli characteristic of each liquid crystal. Eq. (11) is bounded from below if so-called Ericksen's inequalities [60] are met:

$$K_{11} \geq 0, K_{22} \geq 0, K_{33} \geq 0. \quad (12)$$

Thus all deformations are energetically penalized and the nematic remains a stable reference state.

However, it has been less than a quarter of a century since this well-established picture was confronted by the discoveries of novel nematic phases exhibiting unconventional elastic behavior [3, 7, 27, 61], where softening of one of elastic constants occurs. That reorganization of elastic hierarchy is said

²Although we identified an approximate boundary of the crystalline phases, structure identification was beyond the scope of this study.

³In continuum theory, the elastic constants are treated as phenomenological, adjustable parameters.

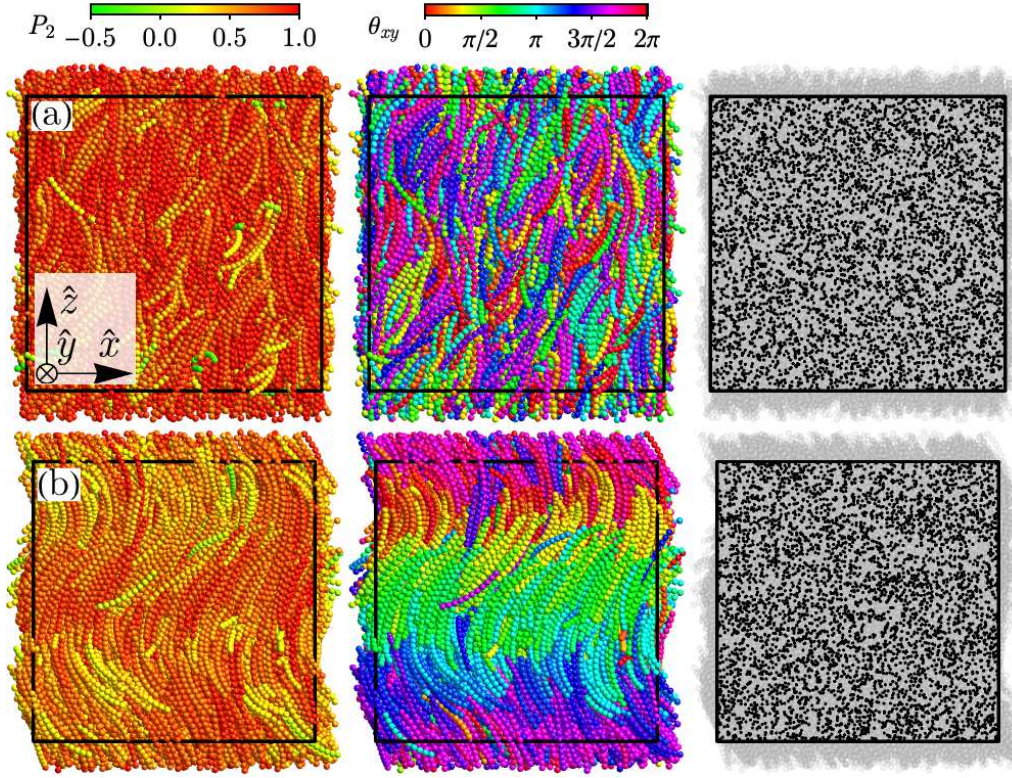


Figure 4: System snapshots of nematic phases: (a) nematic $N(n, \eta) = (10, 0.29)$, and (b) twist-bend nematic $N_{TB}(n, \eta) = (11, 0.33)$. Each panel in a single row corresponds to the same snapshots with different features highlighted: the first column is color-coded according to nematic parameter $P_2(\hat{\mathbf{a}}_i) = 3/2[(\hat{\mathbf{a}}_i \cdot \hat{\mathbf{n}})^2 - 1/3]$, the second one according to counter-clockwise angle θ_{xy} between xy projection of polarization axis $\hat{\mathbf{b}}_i$ and $\hat{\mathbf{x}}$ versor, while the last one shows molecules' mass centers depicted as black dots.

to strongly correlate with the mesogen's molecular shape. For example, for pear-like (wedge-like) shapes K_{11} is the lowest, while for banana-like shapes $-K_{33}$.

Neither pure splay nor bend deformation can fill the two-dimensional space uniformly without frustration (defects). Their appearance can be bypassed by either alternating the bend direction periodically or allowing nonzero twist by lifting the bend into the third dimension. What is more, it is widely believed that splay deformation is inherently coupled with longitudinal molecular polarization, while bend deformation – with transversal polarization [3, 62]. The coupling strongly lowers the values of corresponding elastic constants K_{ii} , which facilitates the formation of modulated phases like splay-bend nematic (N_{SB}) or twist-bend nematic (N_{TB} ; see Fig. 1 as well as Fig. 4b).

The latter, being the focal point of our studies, is characterized by the director field that simultaneously twists and bends in space by precessing on the side of a circular cone that is coaxial with the $\mathbf{z}$ -axis of the laboratory reference frame. As a result, a heliconical structure forms that can be either right- or left-handed due to the SMSB. The director field's modulation can be well described by

$$\hat{\mathbf{n}}_{p,\theta}(x, y, z) = [\sin(\theta) \cos(2\pi z/p), \sin(\theta) \sin(2\pi z/p), \cos(\theta)]. \quad (13)$$

Here, $p = 2\pi/k$ is the pitch, while θ is the tilt angle (half of the cone's opening angle). Polarization is orthogonal to both $\hat{\mathbf{n}}$ and $\mathbf{k} \parallel \hat{\mathbf{z}}$:

$$\mathbf{M}_p(x, y, z) = M \frac{\hat{\mathbf{n}} \times \mathbf{k}}{\|\hat{\mathbf{n}} \times \mathbf{k}\|} = M[\sin(2\pi z/p), -\cos(2\pi z/p), 0], \quad (14)$$

where polarization modulus M corresponds to planar order parameter $\langle M \rangle$ (Eq. (6)).

We observe that for $n \geq 10$ and with increasing density the N_{TB} is preceded by nematic phase (Fig. 3). Lower and upper phase boundaries of N_{TB} also rise with the decrease of n ; the range in packing fraction also increases – it is $\eta \in [0.34, 0.42]$ for $n = 10$, and $\eta \in [0.24, 0.32]$ for $n = 15$. Near-zero $\langle \tau \rangle$ values (Fig. 6b) and high $\langle P_2 \rangle$ values (Fig. 6a) confirm that it is the nematic. Nematic order parameter is almost constant in the whole range with $\langle P_2 \rangle \approx 0.40$. Importantly, we observe the onset of both local $\langle m \rangle$ (Fig. 6e) and planar $\langle M \rangle$ (Fig. 6d) polarization order; the first one spans from $\langle m \rangle \approx 0.50$ on the lower boundary to $\langle m \rangle \approx 0.80$, while the second one – from $\langle M \rangle \approx 0.30$ to $\langle M \rangle \approx 0.75$.

Solid evidence for N_{TB} is given by the inspection of the numerically obtained director profile⁴ in Fig. 7a, where its $\{x, y, z\}$

⁴The directors were computed from the $\mathbf{Q}$ tensors. The latter were aver-

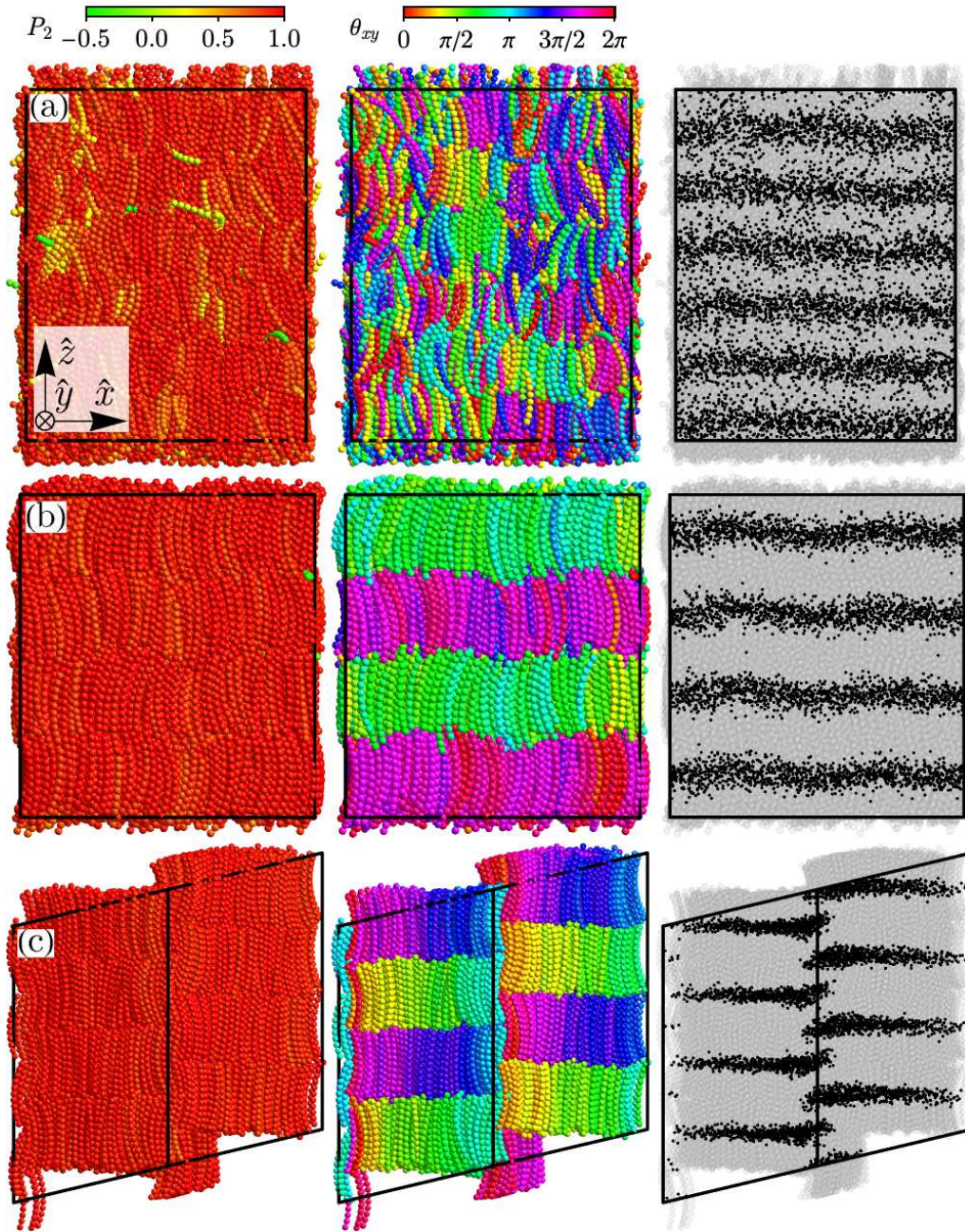


Figure 5: System snapshots of smectic phases: (a) type A smectic SmA $(n, \eta) = (8, 0.37)$, (b) splay-bend smectic Sm_{SB} $(n, \eta) = (10, 0.40)$ and (c) type 1 banana phase B_1 $(n, \eta) = (11, 0.43)$. Each panel in a single row corresponds to the same snapshots with different features highlighted (see Fig. 4). The perspective in panel (c) is such that two edges of the periodic triclinic simulation box coincide into a single segment (the middle vertical one).

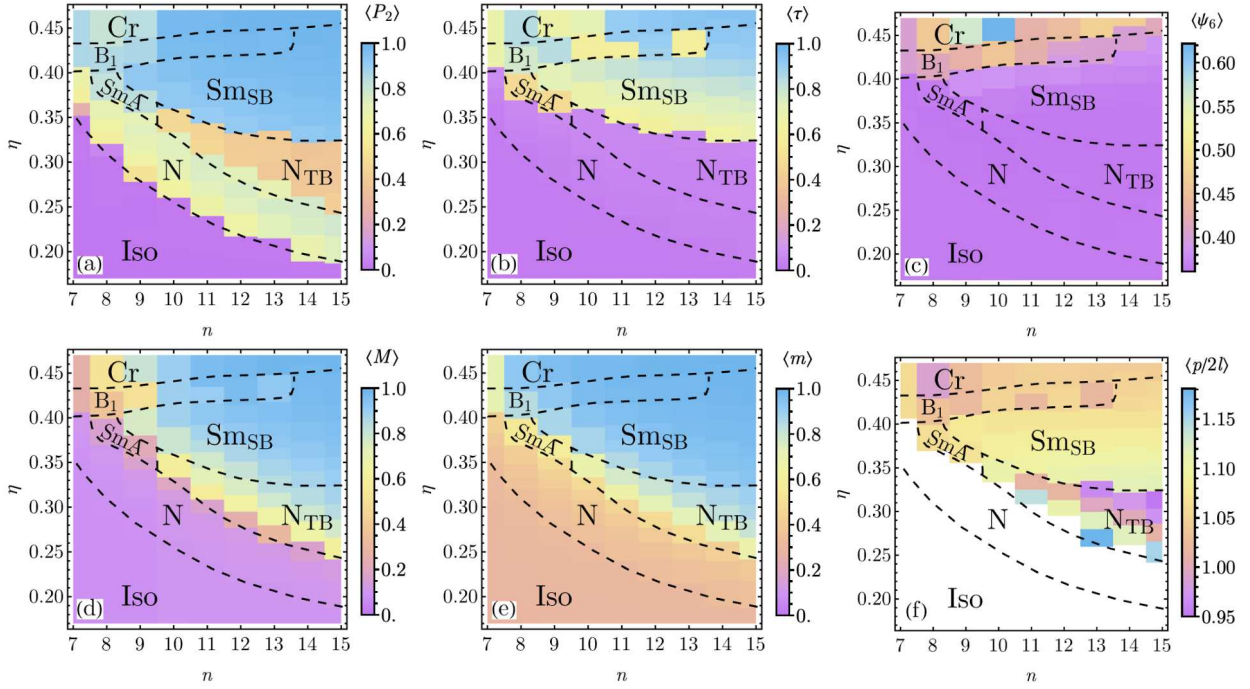


Figure 6: Order parameters and system period as a function of the number of spheres n and packing fraction η : (a) nematic order $\langle P_2 \rangle$, (b) smectic order $\langle \tau \rangle$, (c) local hexatic bond order $\langle \psi_6 \rangle$, (d) planar polarization $\langle M \rangle$, (e) local polarization $\langle m \rangle$ and (f) ratio of half system period and end-to-end molecules length $p/2l$.

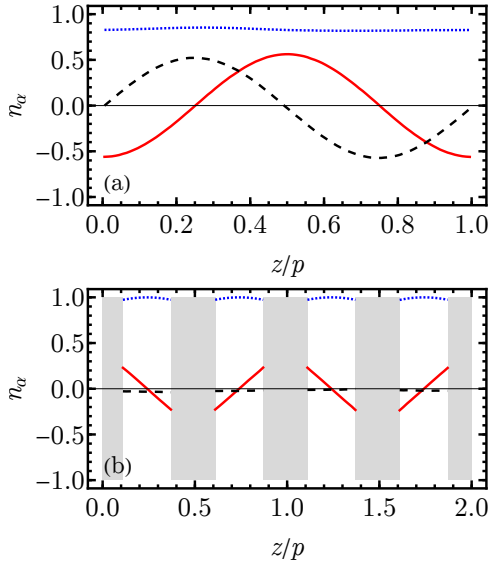


Figure 7: The components n_α ($\alpha = x, y, z$) of the director $\hat{n}$ as a function of the z coordinate (along the wavevector $\mathbf{k}$) for (a) N_{TB} (n, η) = (11, 0.33), and (b) Sm_{SB} (n, η) = (11, 0.40), computed from the numerical simulations. The subsequent components are plotted as: $\alpha = x$ red solid line, $\alpha = y$ black dashed line, and $\alpha = z$ blue dotted line. The gray areas in panel (b) correspond to regions between the layers with hardly any molecules.

components are plotted against the z -coordinate within the simulation box. The n_z coordinate remains constant, while n_x and n_y are sinusoidal with the same amplitude and dephased by a quarter of period, which confirms that the director is precessing around the cone along the structure's wavevector. Fig. 6f shows how p varies with η and n . Likewise for order parameters, the period is nearly constant on both Iso- N_{TB} and N_{TB} - Sm_{SB} phase boundaries and is close to two molecular lengths⁵ $2l$. However, it slightly decreases under compression, with $p/2l \approx 1.15$ on the lower boundary to $p/2l \approx 0.95$ on the upper boundary. The tilt angle θ can be obtained by fitting the relation (13) to the numerical data. The variability of θ is very low – for all simulation points it lies in the range $\theta \in [33.5^\circ, 39^\circ]$. Astonishing is that this result coincides with the experimental outcomes, theoretical predictions and all-atom simulations (see, e.g., [23, 44–46, 64–66]).

Additional information is retrieved from the analysis of the correlation functions (Fig. 8). In all three panels, black and red dashed lines refer to the N_{TB} phase for, respectively, a shorter molecule with $n = 11$, and a longer one with $n = 15$. Both cases are qualitatively similar, however, the amplitudes are larger for $n = 15$, which hints that the orientational fluctuations around the director are more damped with a growing n . The S_{aa}^{220} correlation function (Fig. 8a) measuring nematic-like correlations

⁵aged over multiple system snapshots, accounting for the movement due to the translational Goldstone mode [63].

⁵For real life N_{TB} -forming mesogens the period, with respect to lengths of constituent molecules, varies significantly, e.g. from 0.25 to 4 [31].

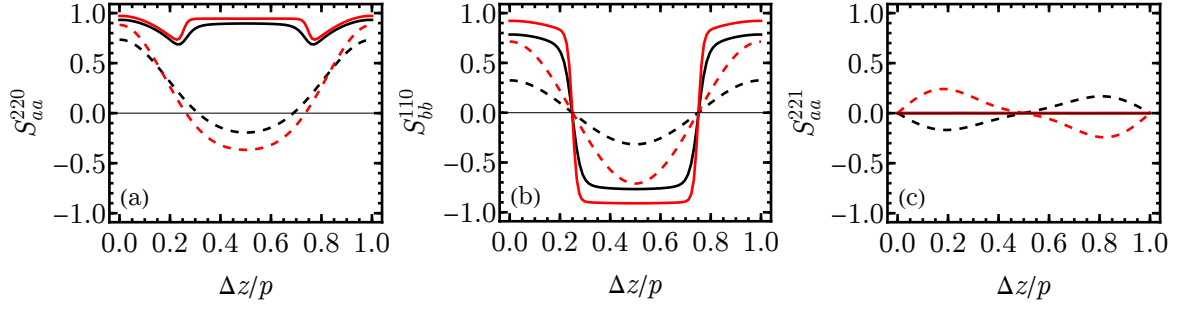


Figure 8: Correlation functions S_{aa}^{ijk} for shorter molecule with $n = 11$: N_{TB} $\eta = 0.32$ (black dashed line), Sm_{SB} $\eta = 0.37$ (black solid line) as well as for longer molecule with $n = 15$: N_{TB} $\eta = 0.29$ (red dashed line), Sm_{SB} $\eta = 0.39$ (red solid line). The subsequent panels show (a) S_{aa}^{220} , (b) S_{bb}^{110} , and (c) S_{aa}^{221} correlation functions against the ratio of distance along the z axis and structure's period.

falls well below zero for $\Delta z = p/2$, when the directors lie on the opposite side of the precession cone. The S_{bb}^{110} correlation function (Fig. 8b), which probes the polarization, follows the oscillating pattern (*cf.* Eq. (14)). Finally, it can be stated that the system is chiral based on the S_{aa}^{221} correlation function (Fig. 8c), which determines whether chirality is present.

Importantly, for $n = 8$ and 9 , the N_{TB} phase is replaced by SmA as indicated by high $\langle P_2 \rangle$ and $\langle \tau \rangle$, along with low $\langle M \rangle$ and moderate $\langle m \rangle$ values, as seen in Fig. 6, as well as by the visual inspection of the system's snapshot (Fig. 5(a)). No director modulation is observed. Local polarization correlations are visible, as confirmed by $\langle m \rangle \approx 0.5$, which is a value higher than for non-polar Iso and N phases but lower than the rest of polar phases. On the other hand, near zero $\langle M \rangle$ excludes the presence of long-range polar order.

Directly above the N_{TB} and SmA a polar smectic is observed, as indicated by high values of all: $\langle P_2 \rangle$, $\langle \tau \rangle$, $\langle M \rangle$, and $\langle m \rangle$ order parameters. The phase is present for $n \in [9, 15]$ and its range widens from $\Delta\eta \approx 0.03$ for $n = 9$ to $\Delta\eta \approx 0.13$ for $n = 15$. System snapshot (Fig. 5b) reveals that the phase is actually antipolar (antiferroelectric). The director averaged over the whole layer is constant and orthogonal to the layers, the direction of the averaged polarization is also constant, but parallel to the layers, however at the same time its sense changes size in an alternating manner.

In the literature, such phase is denoted as the antiferroelectric type A smectic ($SmAP_A$). However, the structure in our system is slightly more complicated, with a visible modulation of the director field, as shown in Fig. 7b. Notably, there are hardly any molecules between the layers (gray areas on the plot), thus the director field is well-defined only in the finite range around the middle of the layer. It is clear, that the director performs oscillatory movement in the xz plane and has a near-zero y component, thus we will rather refer to this phase as splay-bend smectic (Sm_{SB}).

The director field for splay-bend nematics and smectics can be well described by

$$\hat{n}_{p,\theta}(x, y, z) = [\sin(\theta) \cos(2\pi z/p), 0, \sqrt{1 - \sin^2(\theta) \cos^2(2\pi z/p)}]. \quad (15)$$

Such relation fits well to the simulation data and enables us

to establish the oscillation angle θ (the opening angle of the flattened cone). Similar to the tilt angle in the N_{TB} phase, the variability of θ is rather low, $\theta \in [14^\circ, 19^\circ]$. The width of the layer, corresponding to the half structure period, is presented in Fig. 6f. It is close to the molecule's length and slowly decreases under compression with $p/2l \approx 1.12$ at the lower boundary to $p/2l \approx 1.04$ at the upper one.

Both Eq. (13) and Eq. (15) can be generalized to the precession around a deformed cone with all three (twist, splay, and bend) deformations present:

$$\hat{n}_{p,\theta_x,\theta_y}(x, y, z) = \left(\frac{\sin(\theta_x) \cos(2\pi z/p)}{\sqrt{1 - \sin^2(\theta_x) \cos^2(2\pi z/p) - \sin^2(\theta_y) \sin^2(2\pi z/p)}} \right). \quad (16)$$

The structure is parametrized by two different opening angles θ_x and θ_y for, respectively, x and y axes. If $\theta_x = \theta_y = \theta$ it reduces to the twist-bend modulation, Eq. (13), while for $\theta_x = \theta$, $\theta_y = 0$ splay-bend modulation, Eq. (15), is obtained. Interestingly, Chiappini and Dijkstra [14] were able to observe intermediate twist-splay-bend smectic Sm_{TSB} with non-zero $\theta_x \neq \theta_y$ between the N_{TB} and Sm_{SB} . Similar to the previous study [38], this phase is absent in our system; refining the sampling grid around the N_{TB} - Sm_{SB} transition shows that both the order parameters and the packing fraction experience a jump, suggesting that the phase transition may be of the first order.

The correlation functions for shorter ($n = 11$, black solid line) and longer ($n = 15$, red solid line) molecules are shown in (Fig. 8). The nematic-like correlation function S_{aa}^{220} remains high in the whole range since the local tilt of the director with respect to the wavevector remains low (*cf.* the oscillation angle θ not exceeding 20°). The maximum in $\Delta z = 0.5p$ is higher than the ones in $\Delta z = 0, p$, since the tilt is inverted in the adjacent layers (separated by $0.5p$). Minima are observed around $\Delta z \approx 0.25p, 0.75p$. As the high-density areas are rather narrow, this distance corresponds mainly to the correlations between the layers and the space between them containing outliers with anomalous orientations, which, in consequence, lowers the values of S_{aa}^{220} . The polarization correlation function S_{bb}^{110} shows strong correlations between every even number of

layers and strong anticorrelations between every odd number of layers. Contrary to the N_{TB} , it resembles more a square wave than the sinusoidal one. It is due to the fact that for Sm_{SB} , the polarization does not revolve around the circle but, alike the director, performs an oscillatory movement with a similar, small oscillation angle θ . Finally, S_{aa}^{221} is zero, indicating that the structure is non-chiral.

One of the unique features of bent-shaped molecules is the enhanced, shape driven, flexopolarization effect, which is a consequence of the coupling between polarization and strain gradient (splay or bend deformation of the director field) [3]. Due to packing efficiency, especially in the smectic phase, where the molecules are mostly co-planar and their axes parallel, the polarization axes tend to splay [67]. Consequently, sustaining a constant polarization in the xy plane in the Sm_{SB} phase involves the increase in the free energy. On the other hand, as it was mentioned before, splay deformation cannot fill the space uniformly without the defects. For sufficiently large densities, where the packing efficiency grows in importance, the second mechanism becomes energetically favorable, and frustrated structures are formed.

In the spirit of the aforementioned reasoning, we state that the phase presented in Fig. 5c is one of such frustrated structures. It has a high nematic and smectic order (Fig. 6a and b), as well as both local and global polarization order (Fig. 6c and d). Interestingly, local hexatic order $\langle\psi_6\rangle$ is also elevated (Fig. 6f). The structure can be identified as a part of the type 1 banana phase (B_1) family [68]. It is characterized by the mesostructure of hexatically packed columns along the y axis (in the coordinate system of Fig. 5) with discontinuities in the polarization field between them. Polarization axes are parallel to the y axis in the middle of each column and they rotate when one moves away from the center, becoming parallel to the x axis on the boundary. The adjacent columns along the z axes prefer antipolar correlations between the molecules – in the middle, the polarizations are antiparallel. It can be attributed to more compatible vibration motion of the ends of the molecules from the adjacent layers (see Fig. 4 in Ref. [69]), which was also the case for Sm_{SB} .

The phase occurs in a narrow range of packing fractions $\Delta\eta = 0.03$ above $\eta = 0.40$ for $n \in [7, 13]$, shifting slightly towards higher packing fractions with increasing n . The exception is $n = 12$, for which Sm_{SB} forms instead (Fig. 3). Most probably, it is a metastable state in contradiction to B_1 , as these two structures are in direct competition. As the B_1 phase assembles spontaneously when a lower-density Sm_{SB} phase is compressed in a triclinic box, it is highly unlikely that B_1 is metastable with respect to Sm_{SB} for all n . On the other hand, we cannot pinpoint with full certainty the actual range of this phase either in n or η . Notably, the structure borders with three liquid phases: Iso, SmA , and Sm_{SB} . To our best knowledge, such structure was never reported in computational studies, however, similar ones are well known in the experiment [67, 70]. Additionally, we want to remark that the structure was observed in our previous study [38]. We, however, were not able to assess its stability at the time, thus we called it the SmX .

4. Conclusions

By means of hard-particle constant pressure NPT Monte Carlo simulations, we have analyzed the self-assembly of rigid, bent-shaped molecules with fixed bend angle of $\chi = 130^\circ$ and diversified length reflected in the number n ($n \in [7, 15]$) of adjacent spheres. The stability of the liquid crystalline phases was increased with a growing n pushing all Iso- N - N_{TB} - Sm_{SB} boundaries downwards. The twist-bend nematic phase, previously reported for the same molecule with $n = 11$ [37, 38], was superseded by the smectic A phase for $n < 9$, pinpointing $n = 10$ as the shortest (most narrow) molecule, for which the phase is present in the model. The tilt angles for both N_{TB} and Sm_{SB} structures remained nearly constant in the whole corresponding regions and were equal, respectively, around 35° and 17° . For relatively high packing fractions, in the range $\eta \in [0.40, 0.43]$, frustrated type 1 columnar banana phase was observed. It was constructed from hexatically packed columns with polarization splay within them. To our knowledge, no previous computational works reported a similar phase, although it is well known from the experiments (see, e.g., [67, 70]). This phase is onward destabilized for $n \geq 14$ in favor of the Sm_{SB} . It is worth noting that the molecules that form both the twist-bend nematic and banana phases are yet very scarce [71].

This study, together with our previous one [38], helps to understand the importance of both the molecular curvature as well as its length (thickness) for stabilizing the phases with modulations in director and polarization fields. Future studies may entail further exploration of a similar model with smooth, bent spherocylinders instead of multiple spherical beads [14], as well as replacing spheres with oblate spheroids or introducing chirality at the molecular level.

Data availability

The datasets generated during and/or analyzed during the current study are available from P.K. upon reasonable request.

Code availability

The source code of an original simulation package used to perform Monte Carlo sampling is available at <https://github.com/PKua007/rampack>.

Author Contributions

P.K.: Methodology, software, formal analysis, investigation, data curation, writing – original draft, writing – review & editing, visualization, funding acquisition.

W.T.: Conceptualization, methodology, validation, formal analysis, investigation, writing – original draft, writing – review & editing, visualization.

M.C.: Writing – original draft, writing – review & editing, supervision.

Conflicts of interest

There are no conflicts of interest to declare.

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Splay and polar order in a system of hard pear-like molecules: confrontation of Monte Carlo numerical simulations with density functional theory calculations

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Recent experimental discoveries of novel nematic types with polar order, including ferroelectric nematic and splay nematic, have brought the resurgence of the interest in polar and modulated phases. One of the most important factors that is widely believed to be crucial for the formation of new phases is the pear-like shape of mesogenic molecules. Such molecules were treated using second-virial density functional theory in [De Gregorio, P et al., *Soft Matter*, 2016, **12**(23), 5188–5198], where the authors showed that the K_{11} splay elastic constant can become negative due to solely entropic reasons leading to long-range splay and polar correlations. To verify whether the predictions are correct, we performed Monte Carlo simulations of the same hard-core molecules used in the DFT study. As our results suggest, no polar or modulated liquid crystalline phases emerge; polar and splay correlations are either at most short-range or completely absent. On the other hand, a polar ferroelectric splay crystal was observed.

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1 Introduction

Since their discovery in 1888,¹ liquid crystals have become one of the most fruitful areas of study for various phases characterized by unexpected properties resulting from their internal structure based on the orientational order of the anisotropic molecules that built them.^{2–4} The internal structure of liquid crystals leads to their anisotropic macroscopic properties, which are the basis for numerous applications, the most popular of which are liquid crystal displays (LCDs).⁵

The most common and simplest liquid crystalline phases are nematics and smectics, where the director $\hat{n}$ – the direction along which the main axes of the molecules tend to align – is the same in the whole system. Apart from these structures, modulated phases, where the direction of the ordering changes, are of particular interest. Such phases are typically induced by the breaking of specific symmetry at the molecular level, and therefore, instead of parallel alignment of neighboring molecules, a slight tilt in their orientations is preferred; thus, the director is no longer spatially constant. In general, the deformations of a uniform director field are usually described in terms of the Oseen–Zocher–Frank free energy.^{6–8}

$$\mathcal{F}_{\text{OZF}} = \frac{1}{2}K_{11}[\hat{n}(\nabla \cdot \hat{n})]^2 + \frac{1}{2}K_{22}[\hat{n} \cdot (\nabla \times \hat{n})]^2 + \frac{1}{2}K_{33}[\hat{n} \times (\nabla \times \hat{n})]^2. \quad (1)$$

The subsequent terms correspond to, respectively, splay, twist, and bend deformation modes. K_{ii} , called the elastic constants, determine the energetic cost of deviation from a uniform director field. In most scenarios, they are all positive with $K_{22} < K_{11} < K_{33}$,^{9,10} thus any deformations are opposed by restoring torques. There are, however, experimental, theoretical, and numerical cases, where one of them is anomalously low, or even negative.^{11–20} In the latter case, the uniform nematic or smectic ceases to be the stable structure in favor of modulated phases (see Fig. 1). These include cholesterics,²¹ twist-bend nematic N_{TB} ,^{15,16,19,20,22} splay nematic N_{S} ,^{23–26} splay-bend nematic N_{SB} ^{27–30} and smectic Sm_{SB} ^{19,20} as well as splay-twist-bend smectic Sm_{STB} .¹⁹ Of particular interest has recently been the splay nematic N_{S} phase, as it is closely related to the ferroelectric nematic N_{F} ^{31–34} with global polarization, which has been gaining a lot of attention due to its scientific and practical significance.³³

One of the most important factors responsible for the softening of elastic constants is the shape effect. It was repeatedly proven using theoretical models^{17,19,35} as well as molecular dynamics (MD) and Monte Carlo (MC) simulations,^{13,17,19,20} wherein purely repulsive bent-core (banana-shaped) molecules

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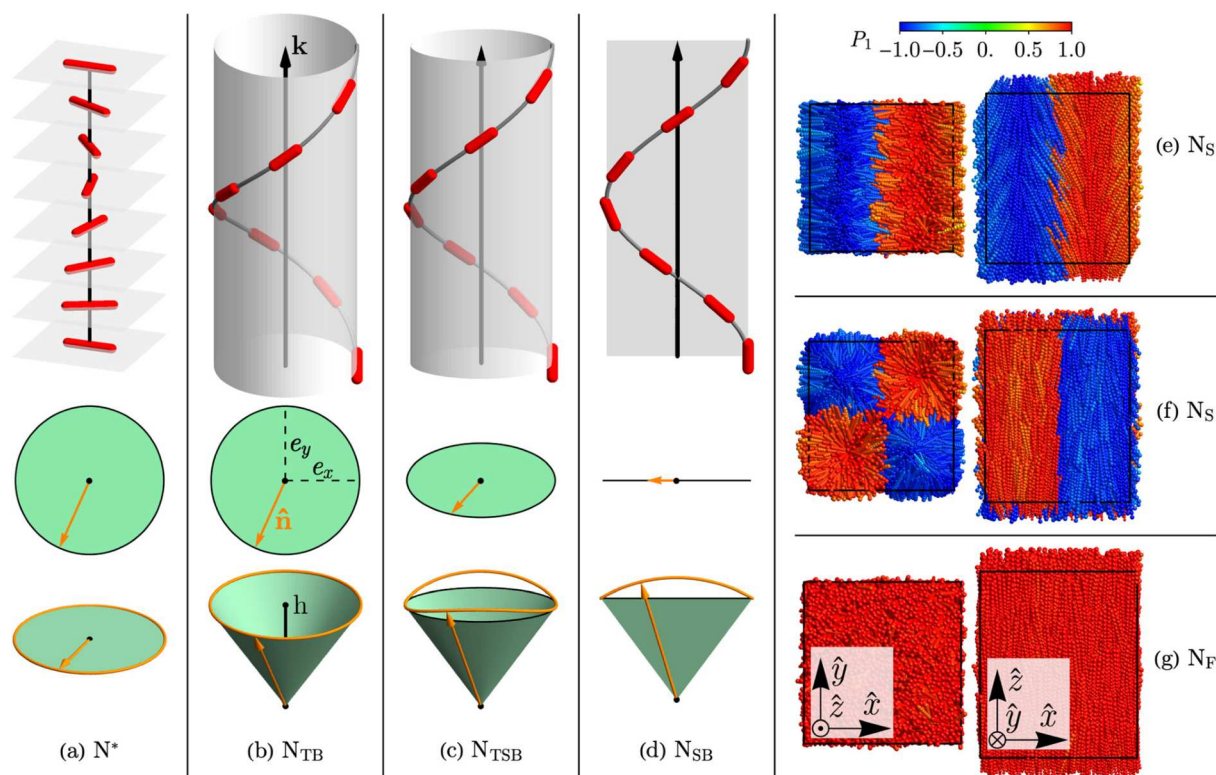


Fig. 1 Schematic representations of selected modulated phases: (a) cholesteric N^* , (b) twist-bend nematic N_{TB} , (c) twist-splay-bend nematic N_{TSB} , (d) splay-bend nematic N_{SB} , (e) single splay nematic N_S , (f) double splay nematic N_S , and (g) ferroelectric nematic N_F . In phases from columns (a)–(d), the director $\hat{n}$ precesses around an asymmetric cone with axes e_x and e_y and height h along the modulation wavevector $\mathbf{k} \parallel \hat{z}$ ($e_x = e_y$, $h = 0$), (b) $e_x = e_y$, $h \neq 0$, (c) $e_x \neq e_y$, $h \neq 0$, (d) $e_x \neq 0$, $e_y = 0$, $h \neq 0$. Within each column, the top graphics illustrates how the preferred direction of molecules changes along $\mathbf{k}$, the middle one shows the top view of the precession cone and the bottom one offers a perspective view of the cone. Panels (e) and (f) show two hypothetical realization of splay nematic: (e) single splay with a striped pattern and (f) double splay with a checkerboard pattern, while (g) is the ferroelectric nematic with spontaneous macroscopic polarization. Within each row, the left panel is the top view, while the right panel is the side view. The color-coding is according to $P_1 = \hat{\mathbf{a}} \cdot \hat{\mathbf{z}}$, where $\hat{\mathbf{a}}$ is the main molecular axis. Please note that all presented phases may theoretically occur in nematic and smectic variants depending on whether density modulation is present or not.

spontaneously form an N_{TB} phase with broken mirror symmetry. One of these works is that of De Gregorio *et al.*,³⁵ which, by means of density functional theory (DFT) calculations, predicts the existence of the N_{TB} phase for banana-shaped molecules, as well as the splay nematic N_S phase for pear-like molecules. Moreover, the onset of spontaneous director field modulation was accompanied by the polar order; in the former case, the bend was linked to the transversal polarization of the molecule, while in the latter case, the splay was linked to the longitudinal polarization. To our knowledge, the N_S phase was not observed in an MD or MC study with purely entropic interactions. On the other hand, polar nematic and polar smectic were observed in MC simulations in the system built of pear-like molecules interacting through a generalized Gay-Berne potential that accounts for broken up-down symmetry. Additionally, it appeared that the additional dipole-dipole interaction does not influence the existence of the polar phases,^{36,37} which contrasts recent experiments.³² However, it is known that the Gay-Berne potential with a dipole at one end of the molecule leads to the formation of a bilayer smectic phase.³⁸

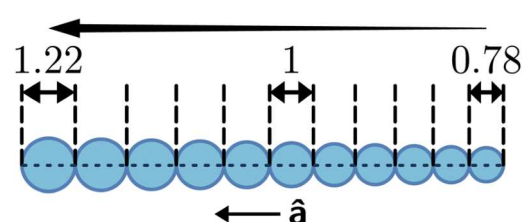


Fig. 2 Illustration of a pear-like molecule used in the study. It consists of eleven co-linear tangent hard spheres with diameters increasing linearly from 0.78 to 1.22. Long molecular axis $\hat{\mathbf{a}}$ points from the smallest to the largest ball. The same model was used in ref. 35.

In this manuscript, we attempt to recreate the splay nematic or the splay smectic phase using MC simulations of the hard-core pear-like model (see Fig. 2). The molecules are built of eleven co-linear tangent hard spheres with diameters linearly increasing from 0.78 to 1.22. The same model was used in ref. 35, where a negative K_{11} splay constant was reported. A similar molecule, with six beads instead of eleven, was the topic of our

previous work.³⁹ As our results suggest, long-range polar and splay orders appear only in the crystalline phase, whereas in the nematic and smectic phase, they are at most present locally.

The article is structured as follows. In Section 2.1, we describe the numerical methods that we were using. Then, in Sections 2.2 and 2.3, we describe the order parameters and pair-correlation functions. Section 3.1 walks through all phases, from the isotropic liquid to the solid state. Finally, Section 3.2 discusses the presence and range of polar and splay correlations in the system, while Section 4 sums up the findings and outlines the potential avenues for future studies. Additionally, Appendix A shows the equilibration curves of the packing fraction and selected order parameters.

2 Methods

2.1 Monte Carlo simulations

To establish the phase sequence for the molecule model under consideration, we performed NpT Monte Carlo simulations^{40–42} of $N = 4320$ molecules using our RAMPACK software.[†] As the interactions are purely hard-core, the only independent thermodynamic parameter is the reduced pressure and temperature ratio $p^*/T^* = pV/k_B T$, where V is the volume of a single molecule and k_B is the Boltzmann constant. We investigated p^*/T^* from the range $[1.0, 11.0]$ corresponding to packing fractions $\eta \in [0.15, 0.51]$, which covered the entire phase sequence, from the isotropic liquid to the solid state. For each p^*/T^* value, we performed a single simulation run consisting of the equilibration phase and the production phase. Both phases lasted around 10^8 Monte Carlo cycles for most p^*/T^* values, however the crystalline phase required extending the equilibration phase to 3×10^8 cycles. In the production phase, instantaneous order parameters and values of pair-correlation functions were computed every 10^5 cycles and averaged at the end. Each cycle consisted of N rototranslation moves, $N/10$ flip moves, and a single box move. In the rototranslation move, a molecule was chosen at random and its position and rotation were perturbed randomly. During the flip move, a random molecule was rotated 180 degrees so that the sense of the molecular axis $\hat{\mathbf{a}}_i$ changed ($\hat{\mathbf{a}}_i \rightarrow -\hat{\mathbf{a}}_i$), while the direction remained unchanged. The flip move facilitated polar order relaxation, especially for high packing fractions. For both types of moves, perturbations were accepted only if no overlap was introduced. During the box move, box vectors $\mathbf{b}_1$, $\mathbf{b}_2$, and $\mathbf{b}_3$ were randomly perturbed and the positions of particles' centers were appropriately updated. Overlapping configurations were rejected immediately, while non-overlapping ones were accepted with a probability given by the Metropolis-Wood criterion.^{40,43}

$$P = \min \left\{ 1, \exp \left(N \log \frac{V_1}{V_0} - \frac{p \Delta V}{T} \right) \right\}, \quad (2)$$

where $V_0 = |\mathbf{b}_1 \cdot (\mathbf{b}_2 \times \mathbf{b}_3)|$ is the box volume before the move, V_1 is the box volume after the move, and $\Delta V = V_1 - V_0$. For

$p^*/T^* < 9.0$ ($\eta < 0.45$), the box was tetragonal and its dimensions were logarithmically scaled, with the z axis perturbed independently of the x and y axes (making the scaling anisotropic). For $p^*/T^* \geq 9.0$ ($\eta \geq 0.45$), the box was triclinic and the box vectors were altered by adding small random vectors to them. Initial configurations for all liquid phases were slightly diluted ($\eta \approx 0.37$) hexagonal honeycomb layers with random up-down orientations of molecules. More precisely, the lattice consisted of $30 \times 18 \times 4$ orthorhombic unit cells with dimensions $0.7 \times 1.2 \times 6.5$, enclosing two unit-volume molecules, whose bounding box midpoints had cell-relative coordinates $(1/4, 1/4, 1/2)$ and $(3/4, 3/4, 1/2)$, with orientations $\hat{\mathbf{a}} = \pm \hat{\mathbf{z}}$. For the crystalline phase at $p^*/T^* = 11$ ($\eta = 0.51$), the initial configuration was the final snapshot of the $p^*/T^* = 8$ ($\eta = 0.44$) smectic A liquid. In all the cases, periodic boundary conditions were used.

2.2 Order parameters

To quantitatively characterize the observed phases, we ensemble averaged five order parameters: nematic order $\langle P_2 \rangle$, smectic order $\langle \tau \rangle$, global hexatic bond order $\langle \Psi_6 \rangle$, local hexatic bond order $\langle \psi_6 \rangle$, and local polarization $\langle P_1 \rangle$. The nematic order parameter P_2 is defined as^{44,45}

$$P_2 = \frac{3}{2} \left(\hat{\mathbf{a}} \cdot \hat{\mathbf{n}} - \frac{1}{3} \right), \quad (3)$$

where $\hat{\mathbf{a}}$ is a molecular axis and $\hat{\mathbf{n}}$ is the director. The mean P_2 in a single snapshot can be conveniently computed using the $\mathbf{Q}$ -tensor:⁴⁵

$$\mathbf{Q} = \frac{1}{N} \sum_{i=1}^N \frac{3}{2} \left(\hat{\mathbf{a}}_i \otimes \hat{\mathbf{a}}_i - \frac{1}{3} \mathbf{I} \right), \quad (4)$$

where the summation consists of all molecules in the system, and $\mathbf{I}$ denotes the unity matrix. In this formulation, P_2 is the eigenvalue of $\mathbf{Q}$ with the highest magnitude, and $\hat{\mathbf{n}}$ is the corresponding eigenvector. Then $\langle P_2 \rangle$ is calculated by averaging it over uncorrelated system snapshots.[‡]

The smectic order parameter can be defined as⁴

$$\langle \tau \rangle = \left\langle \frac{1}{N} \left| \sum_{i=1}^N \exp(i\mathbf{k} \cdot \mathbf{x}_i) \right| \right\rangle, \quad (5)$$

where $\mathbf{k}$ is the smectic wavevector, $\mathbf{x}_i$ is the position of the i -th molecule, $\langle \dots \rangle$ is ensemble averaging, and i is the imaginary unit. In a finite system, $\mathbf{k}$ must be compatible with periodic boundary conditions. In general, one can use the following formula to enumerate all possibilities:

$$\mathbf{k} = h\mathbf{g}_1 + k\mathbf{g}_2 + l\mathbf{g}_3. \quad (6)$$

Here, $\mathbf{g}_i$ is the reciprocal box vector⁴⁶ and h , k , and l are integers (the Miller indices). In this study, all initial states had four layers stacked along the z -axis, therefore, we assumed $hkl = 004$.

[‡] By *uncorrelated system snapshots*, we refer to snapshots whose cycle numbers differ by more than the correlation time estimated using an exponential fit to the correlation function of a given observable.

[†] <https://github.com/PKua007/rampack>

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To quantify hexatic order, one can use the hexatic bond order parameter $\langle\psi_6\rangle$.⁴⁷ It is essentially a two-dimensional parameter; thus, its computation has to be restricted to a single plane in a three-dimensional system. A natural choice is to compute it for each layer separately and sum it over all layers:

$$\langle\Psi_6\rangle = \left\langle \frac{1}{N} \sum_{l=1}^4 \sum_{i=1}^{N_l} \frac{1}{6} \sum_{j \in 6\text{NN}(i)} \exp(6i\theta_{ij}) \right\rangle. \quad (7)$$

Here, N_l is the number of molecules in the l -th layer, θ_{ij} is an angle between the projection of the vector joining i -th and j -th molecules onto the layer and an arbitrary direction within that layer, $\sum_{j \in 6\text{NN}(i)}$ is the summation over six nearest neighbors of

the i -th molecules, $\sum_{i=1}^{N_l} \dots$ is the summation of all molecules in the l -th layer, while $\sum_{l=1}^4 \dots$ is the summation of all molecules in the four layers. The value of Ψ_6^l ranges from 0 for a disordered system to 1 for a perfect hexagonal arrangement.

$\langle\Psi_6\rangle$, which we will call a global hexatic order parameter, is sensitive to relative orientations of hexatic structures in different system domains and is lowered when phase differences are present. Thus, we additionally define local hexatic order parameter:

$$\langle\psi_6\rangle = \left\langle \frac{1}{N} \sum_{l=1}^4 \sum_{i=1}^{N_l} \frac{1}{6} \sum_{j \in 6\text{NN}(i)} \exp(6i\theta_{ij}) \right\rangle, \quad (8)$$

where the modulus is computed after the summation over nearest neighbors. Consequently, $\langle\psi_6\rangle$ quantifies the hexatic order of nearest neighbors of each molecule separately. The maximal value $\langle\psi_6\rangle = 1$ is achieved for a perfect hexagonal arrangement, while for a set of random points $\langle\psi_6\rangle \approx 0.37$.

As the computation of both $\langle\Psi_6\rangle$ and $\langle\Psi_6\rangle$ requires well-defined layers, they will be quantified only for the density-modulated (smectic and crystalline) phases.

To measure local polarization, one can define the following quantity

$$\langle P_1^{(r)} \rangle = \left\langle \frac{1}{N} \sum_{i=1}^N \frac{1}{r+1} \left| \sum_{j \in r\text{NN}, i} \hat{\mathbf{n}}_i \cdot \hat{\mathbf{a}}_j \right| \right\rangle. \quad (9)$$

Here, $(r\text{NN}, i)$ is a set containing particle i and its r nearest neighbors, and $\hat{\mathbf{n}}_i$ is the local director computed for this set using the $\mathbf{Q}$ tensor (4). Locality can be controlled by rank r . The rank should be small to capture correlations on the scale of couple of molecules, however too low values are sensitive to fluctuations. We found that $r = 9$ is a good compromise. $\langle P_1^{(9)} \rangle$ reaches 1 when molecules' polarizations are identical. Using the modulus, the value of $\langle P_1^{(9)} \rangle$ for random polarizations is non-zero and depends on r ; for $r = 9$, it is $\langle P_1^{(9)} \rangle \approx 0.17$. For our convenience, in the next parts of the manuscript, we will write $\langle P_1 \rangle$ without the rank.

2.3 Correlations

As postulated in ref. 35, a splay deformation mode is linked to a longitudinal polarization of the molecule. Thus, we should be looking for a long-range order in the polarization field and splay correlations. To probe polarization correlations, we used the transversal $S_{\perp}^{110}(r_{\perp})$ pair-correlation function.⁴⁸ It is defined layer-wise, similar to ψ_6 :

$$S_{\perp}^{110}(r_{\perp}) = \left\langle \frac{1}{4} \sum_{l=1}^4 \langle \hat{\mathbf{a}}_{il} \cdot \hat{\mathbf{a}}_{jl} \rangle_{i,j,l} \right\rangle, \quad (10)$$

where l is the layer number, $\langle \dots \rangle_{i,j,l}$ denotes averaging over all pairs (i,j) of molecules within the l -th layer, whose transversal distance $r_{\perp}$ lies in the range $[r_{\perp} - dr, r_{\perp} + dr]$ and $2dr$ is the numerical bin size. The transversal distance $r_{\perp}$ is calculated along the layers – more precisely, it is the length of the projection of the vector $\mathbf{x}_{ij} = \mathbf{x}_j - \mathbf{x}_i$ joining molecules i and j onto the nearest layer. In the nematic phase with no density modulation, $r_{\perp}$ could be computed by projecting all molecules onto a single plane. However, in order to facilitate capturing local correlations, we divide nematic snapshots arbitrarily into four layers, whose width is similar to the molecule's length and use the same formula (10) as for modulated phases.

Quantifying splay deformation is significantly more difficult. The reason is that contrary to all the observables introduced earlier, the splay term is a derivative of the director field itself. Thus, to compute it numerically, a sufficiently smooth vector field estimation is needed. This requires ensemble averaging of the field prior to computation. If a long-range order is not present, instantaneous short-range correlations evolve with time, which, with the help of the translational Goldstone mode, average out to a uniform, nematic-like director field. In order to probe local splay correlations, we propose a different scheme. To construct it, we recall that the ideal director field with only the splay deformation and a single singularity in the origin is

$$\hat{\mathbf{n}}(\mathbf{R}) = \frac{\mathbf{R}}{||\mathbf{R}||}, \quad (11)$$

which can be described as a hedgehog-like structure. To distinguish this model from the actual director field observed in the simulations, the distance in the former case is denoted using the capital $\mathbf{R}$, while for the latter one, we continue to use lowercase $\mathbf{r}$. Consequently, here, $\mathbf{R}$ is the vector joining hedgehog singularity with a given point. If we choose a point $\hat{\mathbf{n}} = \hat{\mathbf{n}}(\mathbf{R})$ and move in a transverse direction by $\mathbf{R}_{\perp}$, $\mathbf{R}_{\perp} \perp \mathbf{R}$, arriving at $\hat{\mathbf{n}}' = \hat{\mathbf{n}}(\mathbf{R} + \mathbf{R}_{\perp})$, the angle between $\hat{\mathbf{n}}$ and $\hat{\mathbf{n}}'$ should be approximately a linear function of $||\mathbf{R}_{\perp}||$, as long as $||\mathbf{R}_{\perp}|| \ll ||\mathbf{R}||$. Based on this ideal model and assuming that the tilt within the layers remains sufficiently small, we define $P(\theta|r_{\perp})$ as a conditional probability distribution of finding two molecules i and j with a transversal distance $r_{\perp}$, whose molecular axes form angle $\theta = \cos^{-1} |\hat{\mathbf{a}}_i \cdot \hat{\mathbf{a}}_j|$ (which respects $\hat{\mathbf{n}} \leftrightarrow -\hat{\mathbf{n}}$

director symmetry), normalized as

$$\int_0^\pi P(\theta|r_\perp) d\theta = 1 \quad \forall r_\perp. \quad (12)$$

Then, the local splay correlation should manifest itself as a set of maxima of $P(\theta|r_\perp)$ as a function of both θ and $r_\perp$, for which θ and $r_\perp$ are linearly dependent. Finally, we note that $P(\theta|r_\perp)$ can be computed in the nematic phase by manually partitioning the box into layers in the same way as it was described for $S_\perp^{110}(r_\perp)$ [eqn (10)].

3 Results

3.1 Phase sequence

Fig. 3 shows the phase sequence as well as the order parameters and p^*/T^* ratio as a function of the packing fraction η obtained from the Monte Carlo simulations. A precise determination of the orders of phase transitions is beyond the scope of this work, so the regions in the vicinity of transition points are shown using a hatch filling. The following phases were observed: isotropic (Iso), nematic (N), smectic A (SmA), and ferroelectric double-splay crystal ($\text{Cr}_{\text{DS}}\text{P}_\text{F}$). The system snapshots for all phases, except Iso, are shown in Fig. 4.

At the lowest densities, below $\eta = 0.2$, a disordered isotropic liquid is formed. It then undergoes a phase transition to the nematic phase [see Fig. 4(a)], as indicated by the sharp jump in both the η and the nematic order $\langle P_2 \rangle$ parameter (black solid lines in Fig. 3). It may suggest that the transition is of first

order. No smectic order is observed, as indicated by the smectic $\langle \tau \rangle$ order parameter (red dashed line) – it is close to zero in the entire range of the nematic phase. The nematic order increases monotonically from $\langle P_2 \rangle = 0.8$ for $\eta = 0.23$ to $\langle P_2 \rangle = 0.95$ for $\eta = 0.32$. Such high $\langle P_2 \rangle$ values are above the typical range $\langle P_2 \rangle \in [0.3, 0.7]$ typically observed in experiments,⁴⁹ but they are not uncommon for hard-core systems treated numerically.^{20,39,50,51} In particular, as shown in Fig. 4(a) and discussed in detail in the next section, no long-range splay or polar order is present in the system. Local polarization $\langle P_1 \rangle$ is larger than in the iso phase ($\langle P_1 \rangle \approx 0.25$ compared to $\langle P_1 \rangle \approx 0.17$) and rises very slowly with η . It, however, remains low in the whole range of the N phase.

Around $\eta = 0.33$, an N-SmA phase transition occurs. The snapshot of the SmA phase can be seen in Fig. 4(b). Nematic order $\langle P_2 \rangle$ remains high and a rather quick ascent in $\langle \tau \rangle$ value to $\langle \tau \rangle = 0.8$ can be clearly seen. In experimental setups, the N-SmA phase transition can be both of the first and second order,⁵² however, for idealized hard-core interactions, the former one is usually observed.^{51,53,54} In our simulation data, η did not experience a sudden jump and $\langle \tau \rangle$ rose fast, however smoothly, which would suggest a second-order phase transition. The smectic order $\langle \tau \rangle$ increases up to $\langle \tau \rangle = 0.94$ near the SmA- $\text{Cr}_{\text{DS}}\text{P}_\text{F}$ phase transition. At the same time, the local hexatic bond order $\langle \psi_6 \rangle$ rises almost linearly from $\langle \psi_6 \rangle = 0.4$ at the lower phase boundary to $\langle \psi_6 \rangle = 0.55$ at the top. A higher local hexatic order facilitates a more optimal packing, allowing the system to achieve a more optimal packing fraction η . On the other hand, $\langle \psi_6 \rangle = 0.55$ is still lower than in systems with long-range hexatic order, where the values $\langle \psi_6 \rangle > 0.7$ are observed.³⁹ In the whole range, the global hexatic order parameter $\langle \Psi_6 \rangle$ is near zero; thus, it is omitted in Fig. 3. It confirms the absence of the hexatic smectic phases in the model. Contrary to the nematic phase, the SmA system snapshot Fig. 4(b) reveals some amounts of splay and polar order; however, it appears to be rather short-ranged. Local polarization order is confirmed by the $\langle P_1 \rangle$ value, which rises with the packing fraction η and reaches $\langle P_1 \rangle \approx 0.45$ near the SmA- $\text{Cr}_{\text{DS}}\text{P}_\text{F}$ phase boundary.

Above $\eta = 0.46$, the system freezes and the ferroelectric double-splay crystal ($\text{Cr}_{\text{DS}}\text{P}_\text{F}$) phase emerges [cf. Fig. 4(c)]. This phase transition is marked by a sharp jump in η , $\langle \psi_6 \rangle$ and $\langle P_1 \rangle$, along with a slight decrease of $\langle P_2 \rangle$ and $\langle \tau \rangle$. The phase was first observed and discussed in detail in ref. 39, where a similar system of pear-like molecules was considered; however, the molecules were built of six instead of eleven beads. Here, we only give a brief summary. The phase is built up of layers. Within each layer, we observe square clusters of molecules with the same polarization, either “up” [$P_1 > 0$, colored red in Fig. 4(c)] or “down” [$P_1 < 0$, colored blue]. These clusters are arranged in a chessboard-like long-range pattern. Local polarization in clusters is high with $\langle P_1 \rangle$ reaching 0.89. The molecules within each cluster form an ordered hexatic crystal with a high local bond order $\langle \psi_6 \rangle = 0.7$. Global bond order reaches $\langle \Psi_6 \rangle = 0.51$. Its value is significantly lower than $\langle \psi_6 \rangle$, which suggests that hexatic structures within different clusters are not always in phase. Long-range splay deformation is also clearly

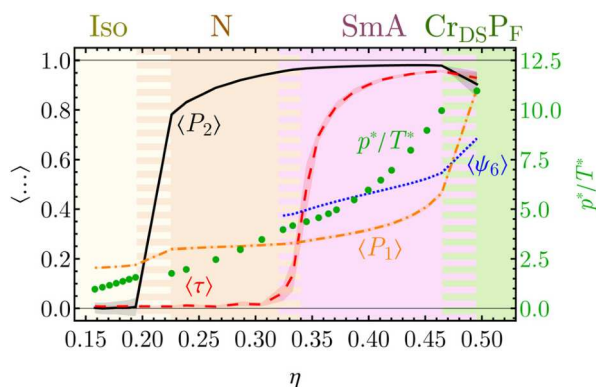


Fig. 3 Phase sequence as a function of packing fraction η . The colored areas represent the ranges of subsequent phases, as labeled above the diagram: Iso (isotropic), N (nematic), SmA (smectic A), and $\text{Cr}_{\text{DS}}\text{P}_\text{F}$ (ferroelectric double-splay crystal). The lines in the graph depict the dependence of order parameters on η : nematic order $\langle P_2 \rangle$ (black solid), smectic order $\langle \tau \rangle$ (red dashed), local hexatic bond order $\langle \psi_6 \rangle$ (blue dotted) and local polarization $\langle P_1 \rangle$ (orange dot-dashed). The green circles represent the equation of state $p^*/T^*(\eta)$ with each point corresponding to one simulated system. Its error is under 0.001, thus error bars are not shown. The left vertical axis, labeled “...” in black, pertains to order parameters, while the right axis, labeled “ p^*/T^* ” in green, corresponds to the equation of state. The hatched regions indicate the vicinity of phase transitions. The shaded areas around the lines denote sample standard deviations of the observables; for the majority of points, the errors are comparable with the width of the curves, thus making them barely visible.

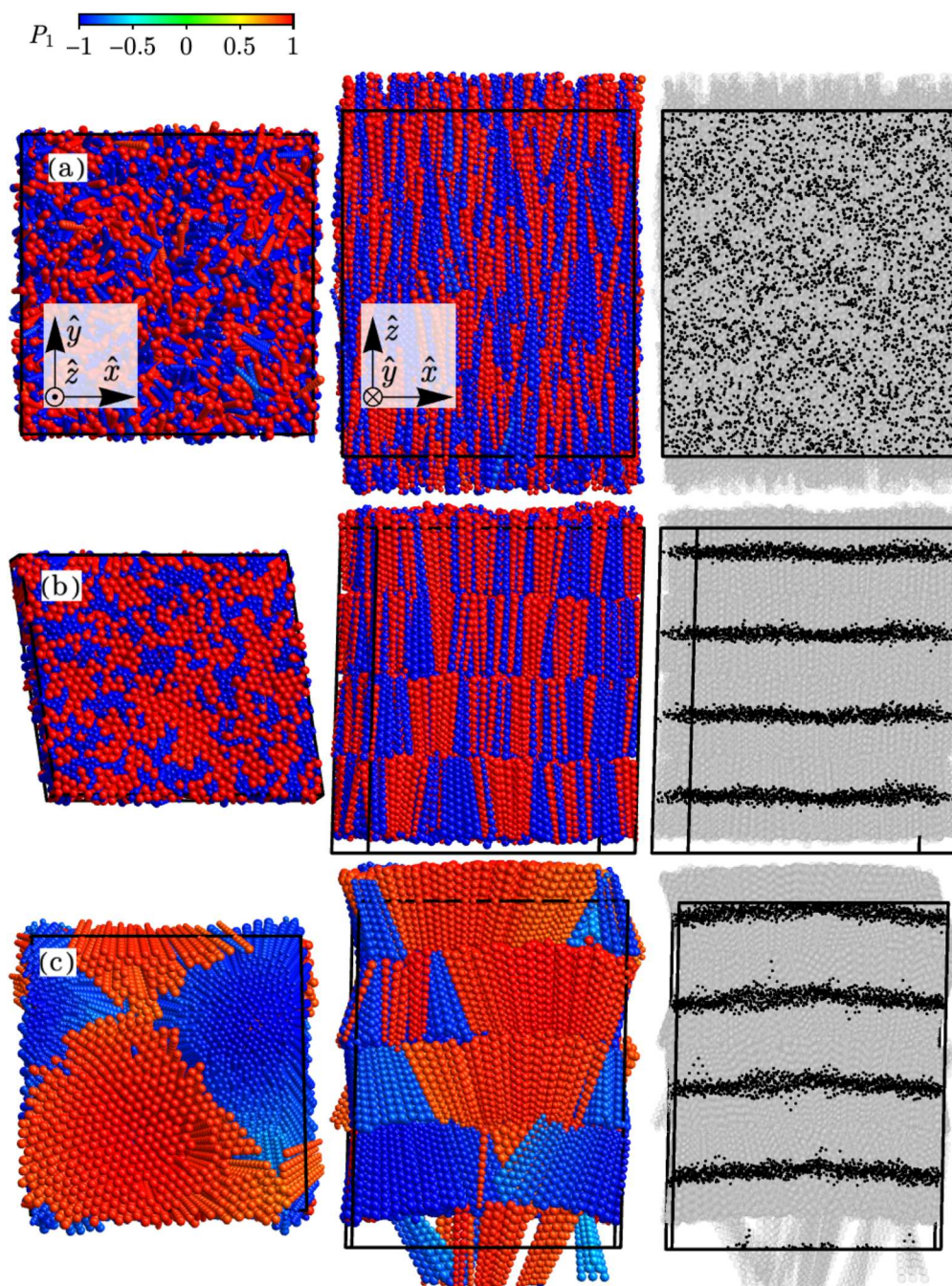


Fig. 4 System snapshots for all observed phases apart from the isotropic liquid: (a) N ($\eta = 0.32$), (b) SmA ($\eta = 0.45$), and (c) CrDsPf ($\eta = 0.51$). Each row depicts different aspects of a single snapshot. The first column shows the top view of the simulation box, the second one shows the front view, and the last one shows the geometric centers (black dots) of molecules overlaid on top of the side view (the second column). The molecules in the first two columns are color coded according to $P_1 = \hat{\mathbf{a}}_i \cdot \hat{\mathbf{z}}$.

visible – the molecules orient in a hedgehog-like pattern discussed in Section 2.3. The presence of splay deformation weakens the global nematic and smectic order, as confirmed by lowered $\langle P_2 \rangle = 0.9$ and $\langle \tau \rangle = 0.92$ values, as compared to $\langle P_2 \rangle = 0.97$ and $\langle \tau \rangle = 0.95$ in the dense SmA phase. Between the

clusters, there are sharp domain walls, where the signs of both polarization and splay vector $\hat{\mathbf{n}}(\nabla \cdot \hat{\mathbf{n}})$ change abruptly. The “chessboard” layers are stacked on each other, matching the signs of polarization and splay deformation between them – as a consequence, polarization domains form long columns

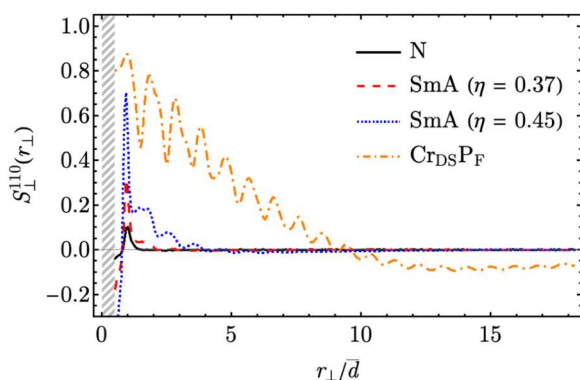


Fig. 5 Layer-wise transversal pair-correlation $S_{\perp}^{110}(r_{\perp})$ function for nematic (black solid line), low-density smectic A (red dashed line), high-density smectic A (blue dotted line) and ferroelectric double-splay crystal (orange dot-dashed line) as a function of transversal distance $r_{\perp}$. $\bar{d} = 1$ is the average diameter of balls building the pear-like molecule.

orthogonal to layers.[§] However, it is important to note that more defects were observed in this system compared to pear-like molecules built of six balls in ref. 39.

3.2 Polar order and splay deformation

As noted in the introduction, the authors in ref. 35 predicted the softening of K_{11} splay constant, when coupling with longitudinal polarization was taken into account. Thus, according to second-order DFT calculations, long-range splay and polar order should emerge. As there does not exist a non-singular director field with only splay deformation [see eqn (11) and ref. 24], it has to be accompanied by other deformations (twist, bend), or the singularities must be allowed. Rosseto *et al.*²⁵ discussed two types of splay nematic N_s .[¶] These structures are presented in Fig. 1(e and f). The first one, already known in the literature,²⁹ was called *single splay nematic* [Fig. 1(e)], where stripes with opposite splay and polarization are stacked in an alternating manner. In the lowest order, polarization and director fields are assumed to be

$$\hat{\mathbf{n}}(x) = (\sin[\Theta(x)], 0, \cos[\Theta(x)]), \quad \Theta(x) = \Theta_0 \sin(\kappa x), \quad (13)$$

$$\mathbf{P}(x) = P_0 \cos(\kappa x) \hat{\mathbf{n}}(x), \quad (14)$$

where Θ_0 determines the strength of the deformation, κ is the structure wavevector, and P_0 is the maximal local polarization. These profiles have been proven to work well near the critical point; however, for lower temperatures, sharper changes are observed.²⁵ The second one was named *double splay nematic* [Fig. 1(f)]. There, columns with opposite splay and polarization form a checkerboard pattern with the fields in the lowest order

[§] In contrast to antiferroelectric splay ($Cr_P A$) and double splay ($Cr_{DS} P A$) crystal phases, where the polarizations are alternating between the layers, see ref. 39.

[¶] This structure has actually both splay and bend modes, however the name *splay-bend* nematic N_{SB} is widely used to describe a different director profile, see Fig. 1(d) and ref. 28

given by

$$\hat{\mathbf{n}}(x, y) = \frac{(\Theta_0 \sin(\kappa x) \cos(\kappa y), \Theta_0 \cos(\kappa x) \sin(\kappa y), 1)}{\sqrt{\Theta_0^2 \sin(\kappa x)^2 \cos(\kappa y)^2 + \Theta_0^2 \cos(\kappa x)^2 \sin(\kappa y)^2 + 1}}, \quad (15)$$

$$\mathbf{P}(x, y) = 2P_0 \cos(\kappa x) \cos(\kappa y) \hat{\mathbf{n}}(x). \quad (16)$$

It is important to note that realization of such structures in a physical system would imply a severely hindered diffusion of molecules between “up” and “down” polarization domains as flipping molecule’s polarization at a domain boundary requires passing a high energy barrier, which is a rare event. As DFT calculations from ref. 35 suggest, K_{11} becomes negative for the number density $\rho \approx 0.050$ (see Fig. 3 therein), which corresponds to $\eta_s \approx 0.30$. In our simulations, it is the nematic phase near the N-SmA phase boundary. Thus, long-range polar and splay correlations should be observed for a high-density nematic and in the whole range of the smectic phase. As stated in Section 3.1 and visible in system snapshots, this is not the case. However, local correlations, especially in the smectic phase, seem to be present.

Polar order correlations can be quantified using $S_{\perp}^{110}(r_{\perp})$. The dependence for selected packing fractions is shown in Fig. 5. For a high-density nematic just below N-SmA transition point ($\eta = 0.32$, black solid line), lying above η_s , polar correlations are marginal – they are non-zero only for nearest neighbors ($r_{\perp} \approx \bar{d}$, where $\bar{d} = 1$ is mean ball diameter) with $S_{\perp}^{110} \approx 0.15$. Slightly higher correlations are observed for a low-density smectic A ($\eta = 0.37$, red dashed line). Here, the maximum is $S_{\perp}^{110}(\bar{d}) \approx 0.3$ and the correlations have a slightly longer range, reaching $r_{\perp} \approx 2\bar{d}$. For high-density smectic A, the correlations are more prominent, with maximum $S_{\perp}^{110}(\bar{d}) \approx 0.7$, but still short-ranged, reaching $r_{\perp} \approx 4\bar{d}$. Local maxima lie near integer multiples of $\bar{d}$, which suggests that they correspond to nearest, next-nearest, next-next-nearest, *etc.* neighbors. Long-range correlations appear only after crystallization. For the $Cr_{DS} P A$ phase at $\eta = 0.51$, positive correlations reach $S_{\perp}^{110} \approx 0.87$ and extend as far as $r_{\perp} \approx 9.5\bar{d}$. After that point, the polarizations are anticorrelated, which is in line with the checkerboard pattern visible in Fig. 4(c). Notably, the phase realizes the double splay nematic structure proposed in ref. 25, but as a crystalline phase.

An insight into the range of splay order can be given by the relative probability density $P(\theta|r_{\perp})$ of the angles θ between molecules at a given distance between them $r_{\perp}$. The histograms are shown in Fig. 6. In the nematic phase [Fig. 6(a)], $\theta \approx 10^\circ$ is the most probable angle for most $r_{\perp}$ with high spread. The highest maximum is for nearest neighbors ($r_{\perp} \approx \bar{d}$). Additional local maxima are visible up to $r_p \approx 4\bar{d}$, which gives us the estimated range of angle correlations. It should be noted that this range is slightly higher than for the $S_{\perp}^{110}$ pair-correlation function. For a low-density smectic A [Fig. 6(b)], the histogram is qualitatively similar, with only a quantitative difference. The preferred angle is lower – $\theta \approx 6^\circ$ with a narrower spread. Local maxima oscillations are also present with a similar range

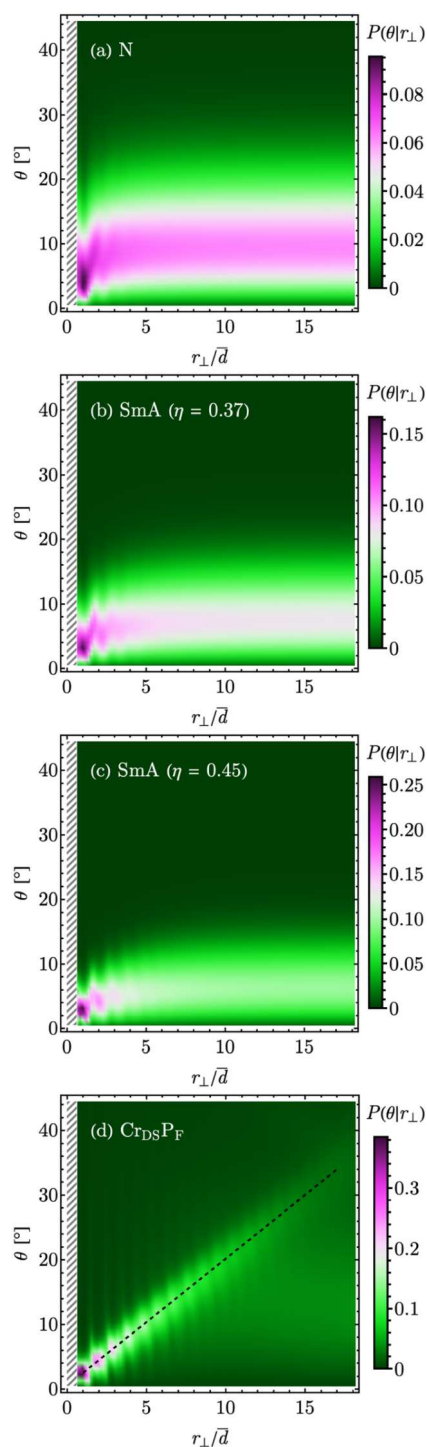


Fig. 6 The evolution of the distribution of angles between the molecules with the transversal distance $r_{\perp}$ between them. For each section with a fixed value of $r_{\perp}$, the maps show a conditional probability density $P(\theta|r_{\perp})$ of finding the two molecules with the angle given by the y-axis value. Subsequent panels correspond to different phases and packing fractions: (a) N ($\eta = 0.32$), (b) SmA ($\eta = 0.37$), (c) SmA ($\eta = 0.45$) and (d) Cr_{DSPF} ($\eta = 0.51$).

of $r_{\perp} \approx 4\bar{d}$. The situation changes slightly for a high-density smectic A [Fig. 6(c)]. Apart from a smaller preferred angle $\theta \approx 5^\circ$ with even less spread than for a low-density smectic, local maxima are narrower and their positions ($r_{\perp}, \theta$) are close to a linear relation – the signature we would expect from splay clusters. Unfortunately, the correlations are short-ranged, spanning up to $r_{\perp} \approx 5\bar{d}$. It changes drastically for the crystalline phase [Fig. 6(d)]. Maxima are clearly visible as far as $r_{\perp} \approx 15\bar{d}$ and they form an almost perfect linear relation given by $\theta = 0.53^\circ + 1.97^\circ r_{\perp}/\bar{d}$. The strength of the maxima diminishes with increasing $r_{\perp}$, as expected, due to the correlations between clusters with opposite polarization. These correlations are also the source of the wide local maximum around $\theta \approx 10^\circ$ for $r_{\perp} > 10\bar{d}$. Between the main maxima, one can observe long vertical lines. They are also likely to originate from off-lattice correlations between adjacent clusters.

As both the visual inspection of system snapshots and the quantitative pair-correlation functions clearly show that both long-range polar order and splay deformation are missing, while at the same time, the DFT calculations predict the N–N_s transition, the question arises of why there is a mismatch between DFT calculations and MC simulations. The first possible reason, which also applies to most theoretical frameworks, is that DFT computations use a second-virial expansion with a correcting Parsons–Lee factor,^{55,56} while MC simulations do not restrict interactions to the two-particle term. Another reason, arguably more probable, is that the authors did not include density modulation in their calculations, while the alleged N–N_s transition point is $\eta \approx 0.30$, which is close to the N–SmA transition point $\eta \approx 0.33$ in our simulations. As second-virial theories often give qualitatively correct results, however, with slightly wrong quantitative predictions,^{||} N_s may have lower free energy than N only over the N–SmA point, where non-modulated smectic A may be favorable over both modulated nematic and smectic phases.

4 Conclusions

We have performed Monte Carlo simulations of hard pear-like molecules built of eleven tangent balls. We scanned a wide range of packing fractions covering the whole phase sequence: isotropic (Iso), nematic (N), smectic A (SmA), and ferroelectric double-splay crystal (Cr_{DSPF}). The phases were classified using visual inspection of simulation snapshots, order parameters, and pair-correlation functions. For the molecule under consideration, second-order DFT calculations³⁵ suggested the existence of a long-range polar and splay order for packing fractions $\eta > 0.30$, which cover high-density nematics and the entire smectic range. Despite the prediction of DFT calculations, no long-range polar or splay order was observed until the system crystallized. Only short-ranged correlations were present in the smectic phase, and in the nematic phase, they were even less

^{||} See for example ref. 17 of the same research group, where theoretical and numerical N–N_{TB} transition points are for number densities, respectively, $\rho \approx 0.056$ and $\rho \approx 0.050$.

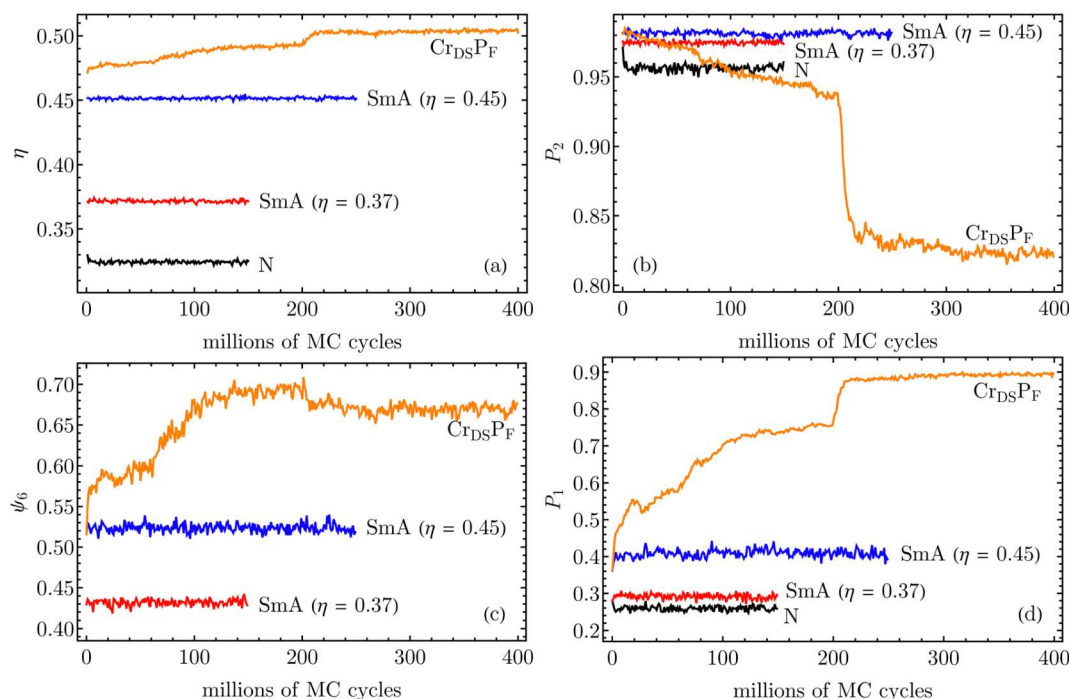


Fig. 7 Equilibration curves of selected quantities: (a) packing fraction η , (b) nematic order parameter P_2 , (c) local hexatic bond order parameter ψ_6 and (d) local polarization P_1 for N ($\eta = 0.32$), low-density SmA ($\eta = 0.37$), high-density SmA ($\eta = 0.45$) and CrDSPF ($\eta = 0.51$).

prominent. The possible reason why the theoretical predictions were not met may be that the theoretical N-N_s transition point is close to the N-SmA point in our study, while at the same time, the smectic order was not included in the previous theoretical work (ref. 35). Another possibility is that the theory is only second-virial. However, since a negative value of the K_{11} splay constant was proved to be theoretically possible, it is worth further exploring other variants of the pear-like molecule model, for example, with a different length or a smooth, convex surface.

Data availability

The datasets generated during and/or analyzed during the current study can be obtained from P.K. upon reasonable request.

Code availability

The source code of an original simulation package used to perform Monte Carlo sampling is available at <https://github.com/PKua007/rampack>.

Author contributions

P. K.: conceptualization, data curation, formal analysis, funding acquisition, investigation, software, visualization, and writing. M. C.: conceptualization and writing.

Conflicts of interest

There are no conflicts to declare.

A Equilibration curves

Fig. 7 shows the equilibration curves for selected quantities: packing fraction η , nematic order parameter P_2 , local hexatic bond order parameter ψ_6 and local polarization P_1 . For nematics and smectics, the system reaches equilibrium relatively fast, not needing more than 2×10^7 MC cycles. On the other hand, the crystalline CrDSPF phase requires significantly more time to develop – the observables reach their thermal values only after 3×10^8 full MC cycles.

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Splay-induced order in systems of hard tapers

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The main objective of this work is to clarify the role that taper-shaped elongated molecules, i.e., molecules with one end wider than the other, can play in stabilizing orientational order. The focus is exclusively on entropy-driven self-organization induced by purely excluded volume interactions. Drawing an analogy to RM734 (4-[(4-nitrophenoxy)carbonyl]phenyl-2,4-dimethoxybenzoate), which is known to stabilize ferroelectric nematic (N_F) and nematic splay (N_S) phases, and assuming that molecular biaxiality is of secondary importance, we consider monodisperse systems composed of hard molecules. Each molecule is modeled using six collinear tangent spheres with linearly decreasing diameters. Through hard-particle, constant-pressure Monte Carlo simulations, we study the emergent phases as functions of the ratio between the smallest and largest diameters of the spheres (denoted as d) and the packing fraction (η). To analyze global and local molecular orderings, we examine molecular configurations in terms of nematic, smectic, and hexatic order parameters. Additionally, we investigate the radial pair distribution function, polarization correlation function, and the histogram of angles between molecular axes. The last characteristic is utilized to quantify local splay. The findings reveal that splay-induced deformations drive unusual long-range orientational order at relatively high packing fractions ($\eta > 0.5$), corresponding to crystalline phases. When $\eta < 0.5$, only short-range order is affected, and in addition to the isotropic liquid, only the standard nematic and smectic-A liquid crystalline phases are stabilized. However, for $\eta > 0.5$, apart from the ordinary nonpolar hexagonal crystal, three additional frustrated crystalline polar blue phases with long-range splay modulation are observed: antiferroelectric splay crystal ($Cr_S P_A$), antiferroelectric double-splay crystal ($Cr_{DS} P_A$), and ferroelectric double-splay crystal ($Cr_{DS} P_F$). Finally, we employ Onsager-Parsons-Lee local density functional theory to investigate whether any sterically induced (anti)ferroelectric nematic or smectic-A type of ordering is possible for our system, at least in a metastable regime.

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I. INTRODUCTION

The most spectacular discovery of the last decade in the field of liquid crystal research has been the identification of the ferroelectric nematic (N_F) [1–4], antiferroelectric nematic splay (N_S) [5], and nematic twist-bend (N_{TB}) [6–8] phases, all characterized by various forms of long-range polar order.

Based on current experimental observations, it seems that the stabilization of these new nematic phases is linked to the strong softening (i.e., reduction by one to two orders of magnitude) of one of the Frank elastic constants, K_{ii} [9], in the parent, uniaxial nematic (N) phase, near the transition to one of the polar nematics. Here K_{ii} s ($i = 1, 2, 3$) weight elementary deformations of splay (K_{11}), twist (K_{22}), and bend (K_{33}) types of the undistorted, reference uniaxial nematic state (N) in the Oseen-Zocher-Frank free energy [9–11]

$$\mathcal{F} = \frac{1}{2V} \int_V [K_{11}[\hat{n}(\nabla \cdot \hat{n})]^2 + K_{22}[\hat{n} \cdot (\nabla \times \hat{n})]^2 + K_{33}[\hat{n} \times (\nabla \times \hat{n})]^2], \quad (1)$$

where $\hat{n}$ denotes the locally preferred orientation of molecules referred to as the director, and V is the system's volume.

While each Frank elastic constant is typically positive and on the order of 10 pN, the observed softening of K_{ii} suggests that the lack of orientational modulation of N is no longer energetically favored, and it can promote the appearance of

orientationally modulated phase. Effectively, it means that the softened elastic constant may become negative. An important observation made by Meyer many years ago [12] was that this softening can be attributed to the entropy of packing of molecules with specific shape of nonzero steric dipole. In fact, the dipolar asymmetry of these molecules is expected to induce a flexopolarization effect, which couples to splay and bend director deformations [13] and effectively reduces the K_{11} and/or K_{33} elastic constants [14]. For instance, molecules with a bow (banana) shape can reduce the K_{33} bend elastic constant, leading to the formation of twist-bend and splay-bent phases [15]. Greco and Ferrarini were the first to explicitly demonstrate this phenomenon through molecular dynamics simulation on a system of bow-shaped molecules that interact solely through steric interactions [16].

Further studies on bow-shaped molecules, focusing on steric interactions, have not only provided successful explanations for the formation of the N_{TB} phase [17,18] but have also demonstrated the potential for stabilizing various intermediate polar states between N_{TB} and N_{SB} [17].

It is well known that even slight differences in the geometry of molecules can have a significant impact on the resulting liquid-crystalline self-assembly. For example, a smectic-A phase is observed in a system consisting of spherocylinders [19], whereas ellipsoids with a very similar shape do not exhibit this behavior [20]. This principle also applies to the recently discovered N_F and N_S phases. These phases rely

on both taperlike molecular anisotropy and a strong, nearly longitudinal total molecular dipole moment as crucial molecular characteristics contributing to their stability. Specifically, the taperlike molecular shapes can result in a negative K_{11} splay constant [21], thereby contributing to the formation of the polar splay nematic [14,22,23] and related smectic phases [24,25].

Numerical simulations of systems composed of wedge-like (e.g., pear-shaped, tapered, etc.) molecules began in the late 1990s [26,27]. In these simulations, shape polarity at the molecular level was induced by a soft interaction potential between molecules, which combined two rigidly connected centers: an ellipsoidal Gay-Berne potential [28] and a spherical Lennard-Jones potential. The reported liquid crystalline phases in these simulations were only ordinary uniaxial nematic and smectic phases, without any macroscopic polarization, as they exhibited a preference for antiparallel local arrangement.

Berardi, Ricci, and Zannoni developed a generalized single-site Gay-Berne potential to model the attractive and repulsive interactions between elongated tapered molecules [29]. Through parameter adjustments and Monte Carlo simulations, they observed stable N_F and ferroelectric smectic liquid crystals. However, while the introduction of a weak axial dipole did not qualitatively impact these observations, an increase in dipole strength resulted in the destruction of long-range ferroelectric ordering. It is worth noting that using a standard Gay-Berne potential with an axial dipole at one end of the molecule resulted in the formation of a bilayer smectic phase [30–32]. Similar mesophase formation was observed in simulations of single-site hard pears [33].

Purely entropic systems constructed of pear-shaped molecules also exhibit a cubic gyroid phase [34,35]. Interestingly, the stability of this phase is highly sensitive to the details of the hard-core interaction. Specifically, the cubic gyroid phase is observed when describing the pear shape using two Bézier curves with the pear hard Gaussian overlap (PHGO) model. However, it vanishes when the hard pears of revolution (HPR) model is used. In the PHGO model, a bilayer smectic phase is also observed, whereas the HPR model exhibits isotropic and nematic phases [36].

Finally, we should mention sno-cone-shaped particles studied using Monte Carlo simulations by Chen, Zhang, and Glotzer [37]. At low packing fractions (0.1–0.3), they observed the self-assembly of molecules into nanoclusters of shape solely determined by the cone angle. The conical excluded volume forced the particles to assemble into curved, closed polyhedral convex shapes.

In this paper, we seek to explore the fundamental mechanisms that can lead to the emergence of long-range splay and potentially polar order in liquid crystal systems. Specifically, we focus on the interactions among hard taper-shaped molecules in the absence of dipolar electrostatic or dispersion forces. By investigating whether such long-range order can be stabilized solely through entropic interactions, we aim to advance our understanding of the essential features of molecular interactions responsible for stabilizing N_F and N_S phases.

To achieve this goal, we utilize a model consisting of six collinear tangent spheres, resulting in a molecule with $C_{\infty v}$ (cone) symmetry [Fig. 1(a)]. The diameters of the spheres fol-

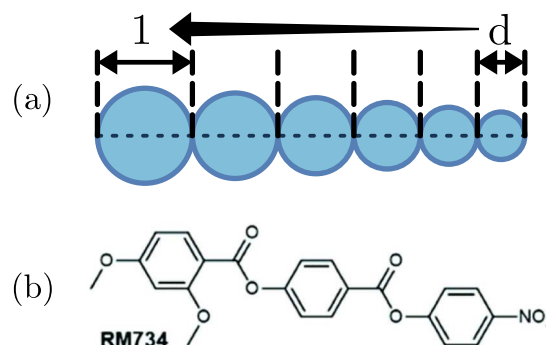


FIG. 1. (a) Family of tapers used in the study; they are built of six collinear tangent spheres with diameters increasing linearly from d to 1 ($d \leq 1$ is a parameter). (b) Taper-shaped RM734 molecule known to form a polar nematic phase. Reprinted from Ref. [4] with the permission of the Royal Society of Chemistry.

low an arithmetic sequence, starting from d and progressing to 1. Specifically, the diameters are given by d , $(4d + 1)/5$, $(3d + 2)/5$, $(2d + 3)/5$, $(d + 4)/5$, and 1. Here, the parameter d represents the diameter of the smallest sphere and serves as a descriptor for the shape of the molecule. When $d = 1$, the molecule reduces to the linear tangent hard-sphere (LTHS) model as described by Vega *et al.* [38]. The molecule's length is equal to $3(d + 1)$, while the mean ball diameter is $(d + 1)/2$. Thus, the molecular aspect ratio is 6 regardless of d . Alternatively, if we use the maximal ball diameter instead of its mean value, the aspect ratio is $3(d + 1)$ and consequently lies in the range $[3, 6]$ for $d \in [0, 1]$.

We have chosen this model to capture essential features of the effective shape exhibited by the RM734 molecule (4-[(4-nitrophenoxy)carbonyl]phenyl-2,4-dimethoxybenzoate) [Fig. 1(b)]. As previously mentioned, the RM734 mesogen has been shown to stabilize N_F and N_S phases [3,4]. By utilizing a model with similar shape characteristics, we aim to gain further insight into the relationship between the entropy of packing and the resulting self-organization in liquid crystal systems. To this end, we investigate the phase diagram and properties of stable structures using Monte Carlo integration. Additionally, we compare our results with those obtained from previous studies on soft- and hard-core pear models. Furthermore, we examine how the gradient of a molecule's diameter influences the presence and extent of the observed phases.

Finally, we recognize that the anisotropic polar shape of the molecules may give rise to nontrivial dense configurations. We are particularly interested in exploring whether these configurations exhibit crystal-like or glasslike structures, considering the potential competition between different types of lattices [39–41].

The remainder of this paper is organized as follows: In Sec. II A we provide a brief description of the Monte Carlo integrator used. In Secs. II B and II C, we introduce the order parameters and correlation functions used to monitor properties of equilibrium structures. The results obtained from Monte Carlo simulations are presented in Sec. III. In Sec. IV, we formulate the Parsons-Lee density functional theory to

study polar ordering in the liquid-crystalline regime. We analyze some equilibrium and metastable phases in detail. Last, we provide a discussion and outlook in Sec. V. The Appendix contains remarks about nontilted hexagonal configurations of close-packed linear tangent hexamers.

II. METHODS

A. Monte Carlo simulations

We assumed hard-core interactions between molecules. The equilibrium phases were classified as a function of the shape parameter d and the packing fraction η . The latter one is defined as a ratio of the total volume of all molecules to the volume of a simulation box, and is a natural choice for purely steric repulsion. System snapshots were obtained numerically using the Monte Carlo (MC) scheme [42] implemented in our RAMPACK software package. Integration was carried out in the N - p - T ensemble. For hard-core interactions, only a ratio p/T of pressure and temperature is an independent parameter and can be used to control the packing fraction η . To allow relaxation of the full viscous stress tensor (including the sheer part), we used a triclinic simulation box with periodic boundary conditions. For a system of N molecules, a full MC cycle consisted of N rototranslation moves, $N/10$ flip moves, and a single box move. In a rototranslation move, a single shape was chosen at random, translated by a random vector, and rotated around the random axis by a random angle (clockwise and anticlockwise rotations were equally probable to preserve the detailed balance condition). If the move introduced an overlap, it was always rejected and accepted otherwise. Flip moves were performed in a similar way to rototranslation moves; however, instead of random translation and rotation, the molecule was rotated by 180° around its geometric center. This type of move facilitated easier sampling of the phase space of the system, especially for high η . For a box move, the three vectors $\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3$ that span the box were perturbed by small random vectors. The move was rejected if any overlaps were introduced. Otherwise, it was accepted according to the Metropolis-Wood criterion with probability [43,44]

$$\min \left\{ 1, \exp \left(N \log \frac{V}{V_0} - \frac{p \Delta V}{T} \right) \right\}, \quad (2)$$

where $\Delta V = (V - V_0)$ and V_0 and V are, respectively, the volume of the box before and after the move. The perturbation ranges were adjusted during the thermalization phase to achieve an acceptance probability of around 0.15. To accelerate simulations in a modern multithreaded environment, we used the domain decomposition technique [45] for molecule moves and we parallelized independent overlap checks for volume moves.

To scan the full phase sequence, from isotropic liquid to crystal, we used p/T ratios corresponding to packing fraction covering $\eta \in [0.3, 0.58]$ for $d \in [0.4, 1.0]$. First, to roughly determine the phase boundaries, preliminary simulations were performed by gradually compressing a small system of $N = 400$ molecules in a cubic box from a highly diluted simple cubic lattice. For each p/T , the integration consisted of the thermalization run with 9.5×10^6 full MC cycles and the production run with 0.5×10^6 cycles to gather averages. The final

snapshot of a run was used as a starting point for the next with a slightly higher p/T . Using the results as guidance, the main simulations were performed on a much larger system with $N > 5000$ in a triclinic box. The initial configuration in the whole range of d was smectic A with $\eta \approx 0.45$ (see Sec. III for the description of phases) prepared by thermalizing different types of slightly diluted crystals for $(1-5) \times 10^8$ cycles. Initial configurations were then independently compressed or expanded to all target densities in parallel. Thermalization runs were performed for $(0.9-4.5) \times 10^8$ cycles, while production runs were performed for $(0.1-0.5) \times 10^8$ cycles. Additionally, in order to estimate maximal packing fractions, the densest configurations for each d were compressed under exponentially increasing pressure for 3×10^8 cycles, reaching $p/T = 10^4$ at the end.

B. Order parameters

Phases in the system can be easily classified using a carefully chosen set of order parameters, whose values have jumps on the boundaries of phase transitions. The nematic order along the director $\hat{\mathbf{n}}$ is detected by the average value $\langle P_2(\hat{\mathbf{a}} \cdot \hat{\mathbf{n}}) \rangle$ of the second-order Legendre polynomial, where $\hat{\mathbf{a}}$ is the long axis of the molecule. Director $\hat{\mathbf{n}}$ can be inferred directly from the system using the second-rank $\mathbf{Q}$ tensor [46], which can be numerically computed as

$$\mathbf{Q} = \frac{1}{N} \sum_{i=1}^N \frac{3}{2} \left(\hat{\mathbf{a}}_i \otimes \hat{\mathbf{a}}_i - \frac{1}{3} \right), \quad (3)$$

where the summation is done over all molecules in a single snapshot. P_2 is then the eigenvalue of $\mathbf{Q}$ with the highest magnitude, and $\hat{\mathbf{n}}$ the corresponding eigenvector. Ensemble-averaged $\langle P_2 \rangle$ is calculated by averaging P_2 over noncorrelated system snapshots. The nematic order parameter has a minimal value -0.5 , when all molecules are perpendicular to $\hat{\mathbf{n}}$, and reaches its maximum 1 for molecules perfectly aligned with $\hat{\mathbf{n}}$ (please note that $\hat{\mathbf{n}}$ and $-\hat{\mathbf{n}}$ directions are equivalent). In a disordered system $\langle P_2 \rangle = 0$.

Density modulation can be quantitatively described by the smectic order parameter $\langle \tau \rangle$ [47]. It is defined as

$$\langle \tau \rangle = \frac{1}{N} \left\langle \left| \sum_{i=1}^N \exp(i\mathbf{k} \cdot \mathbf{r}_i) \right| \right\rangle, \quad (4)$$

where $\mathbf{k}$ is the modulation wave vector compatible with periodic boundary conditions (PBCs) and $\mathbf{r}_i$ is the center of the i th molecule. More precisely, by *molecule's center* we refer to the middle point of a molecule's length. As the drift of the whole system is a Goldstone mode, the absolute value $|\dots|$ is taken before the ensemble averaging to eliminate it. All possible $\mathbf{k}$ can be enumerated using reciprocal box vectors $\mathbf{g}_1, \mathbf{g}_2, \mathbf{g}_3$ [48] and taking linear combinations of them with integer coefficients h, k, l (Miller indices [49]): $\mathbf{k} = h\mathbf{g}_1 + k\mathbf{g}_2 + l\mathbf{g}_3$. Here, as the initial configuration is always a smectic with six layers stacked along the z axis, $hkl = 006$. The smectic order ranges from 0 for a homogeneous system to 1 for a perfectly layered one.

Another feature of the system that is measured in the study is the hexatic order appearing for high packing fractions η , where molecules tend to form hcp-like structures. The local

hexatic order can be measured using the so-called hexatic bond order parameter $\langle\psi_6\rangle$ [50]. For a two-dimensional system, it is defined as

$$\langle\psi_6\rangle = \frac{1}{N} \left\langle \sum_{i=1}^N \frac{1}{6} \left| \sum_{j=1}^6 \exp(6i\phi_{ij}) \right| \right\rangle, \quad (5)$$

where ϕ_{ij} is the angle between an arbitrary axis in the plane and the vector that joins the center of the i th molecule with its j th-nearest neighbor. It can be generalized to three-dimensional systems by projecting the positions of molecules onto the nearest smectic layers and computing ψ_6 within the planes defined by them. Random points give $\langle\psi_6\rangle \approx 0.37$, while a perfect hexatic order yields $\langle\psi_6\rangle = 1$. The local hexatic order can also be computed for a system without layers by projecting all centers on a single plane.

C. Correlation functions

Additional insight into both global properties and supramolecular structures is given by correlation functions. For all correlation functions, the distance is measured between molecules' centers, i.e., midpoints of molecules' lengths. The first is a standard radial distribution function [51], which can be defined in a computationally friendly way as

$$\rho(r) = \left\langle \left\langle \frac{dN(r, r+dr)}{4\pi r^2 dr \cdot (N/V)} \right\rangle_N \right\rangle, \quad (6)$$

where $dN(r, r+dr)$ is the number of molecules whose distance from a selected single molecule lies in the range $(r, r+dr)$, dr is the numerical size of the bin, N is the total number of molecules, and V is the volume of the system. It is then averaged over all molecules, $\langle\cdots\rangle_N$, and over independent snapshots, $\langle\cdots\rangle$. It is normalized in such a way that, for a disordered isotropic system, it approaches 1 for $r \rightarrow \infty$. In systems with long-range translational order, $\rho(r)$ has a series of numerous minima and maxima.

In a layered system, one can also measure the layerwise radial distribution function in the direction orthogonal to $\mathbf{k}$,

$$\rho_{\perp}(r_{\perp}) = \frac{1}{n_L} \left\langle \left\langle \frac{dN_i(r_{\perp}, r_{\perp}+dr_{\perp})}{2\pi r_{\perp} dr_{\perp} \cdot (N/S)} \right\rangle_{N_i} \right\rangle, \quad (7)$$

where n_L is the number of layers, $dN_i(r_{\perp}, r_{\perp}+dr_{\perp})$ is the number of molecules in the i th layer whose distance from a selected single molecule calculated along the layer's plane lies in the range $(r_{\perp}, r_{\perp}+dr_{\perp})$, and S is the total surface area of all layers [52]. In the end, it is averaged over all molecules in the layer, $\langle\cdots\rangle_{N_i}$, all layers, $(1/n_L) \sum_{i=1}^{n_L} \cdots$, and uncorrelated system snapshots, $\langle\cdots\rangle$.

As the results will show, the system develops a nontrivial polar metastructure. To quantify it, we use the layerwise radial polarization correlation [51], defined like $\rho_{\perp}(r_{\perp})$:

$$S_{\perp}^{110}(r_{\perp}) = \frac{1}{n_L} \left\langle \left\langle \sum_{i=1}^{n_L} \langle \hat{\mathbf{a}}_{i_j} \cdot \hat{\mathbf{a}}_{i_k} \rangle_{i_j i_k} \right\rangle \right\rangle, \quad (8)$$

where $\langle\cdots\rangle_{i_j i_k}$ denotes the average over all molecules in the i th layer, whose centers' distance along this layer lies in the $(r_{\perp}, r_{\perp}+dr_{\perp})$ range.

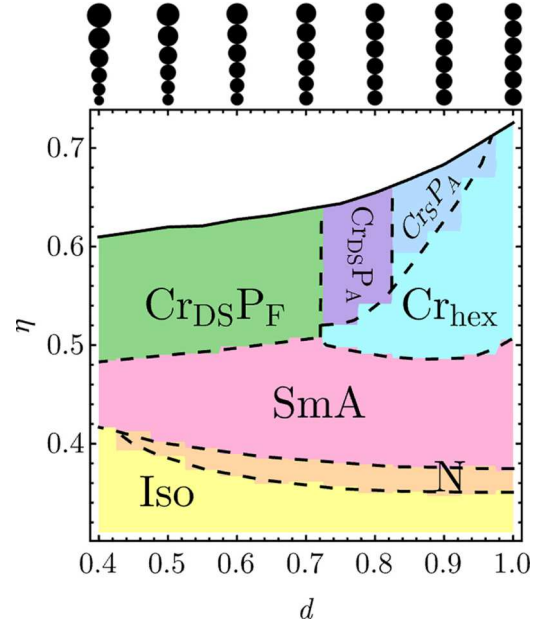


FIG. 2. Phase diagram of the system in (d, η) space. The liquid phases, isotropic (Iso), nematic (N), and smectic A (SmA), as well as crystalline ones, hexagonal crystal (Cr_{hex}), antiferroelectric double-splay crystal ($\text{Cr}_{\text{DS}}\text{P}_A$), antiferroelectric splay crystal (Cr_SP_A), and ferroelectric double-splay crystal ($\text{Cr}_{\text{DS}}\text{P}_F$), were recognized. The black solid line at the top boundary of the phase diagram represents the maximal packing fraction η for a given d value. The illustrative shapes above the diagram were normalized to have the same mean ball diameter.

The range of splay correlations can be quantified by the conditional probability $P(\theta|r_{\perp})$ of finding two molecules with angle θ between their molecular axes $\hat{\mathbf{a}}_i$ at a transversal distance $r_{\perp}$, normalized as

$$\int_0^{90^\circ} P(\theta|r_{\perp}) d\theta = 1, \quad \forall r_{\perp}. \quad (9)$$

To be consistent with the polarization correlation function, this quantity will also be calculated layerwise. As splay corresponds to the radial spread of director field lines, the most probable angle θ should grow with $r_{\perp}$ in systems with nonzero splay deformation mode.

III. RESULTS

Using the method described in Sec. II A, we were able to recognize all phases for $d \in [0.4, 1.0]$ and $\eta \in [0.3, 0.58]$. There are three liquid phases, isotropic liquid (Iso), nematic (N), and smectic A (SmA), and four crystalline phases, hexagonal crystal (Cr_{hex}), antiferroelectric splay crystal (Cr_SP_A), antiferroelectric double-splay crystal ($\text{Cr}_{\text{DS}}\text{P}_A$), and ferroelectric double-splay crystal ($\text{Cr}_{\text{DS}}\text{P}_F$). The phase diagram is presented in Fig. 2, the order parameters are shown in Fig. 3, while Figs. 4–6 contain correlation functions. Moreover, representative equilibrium snapshots of all phases can be seen in Figs. 8 and 9. The phases for all sampled pairs (d, η) were manually classified using order parameters and visual

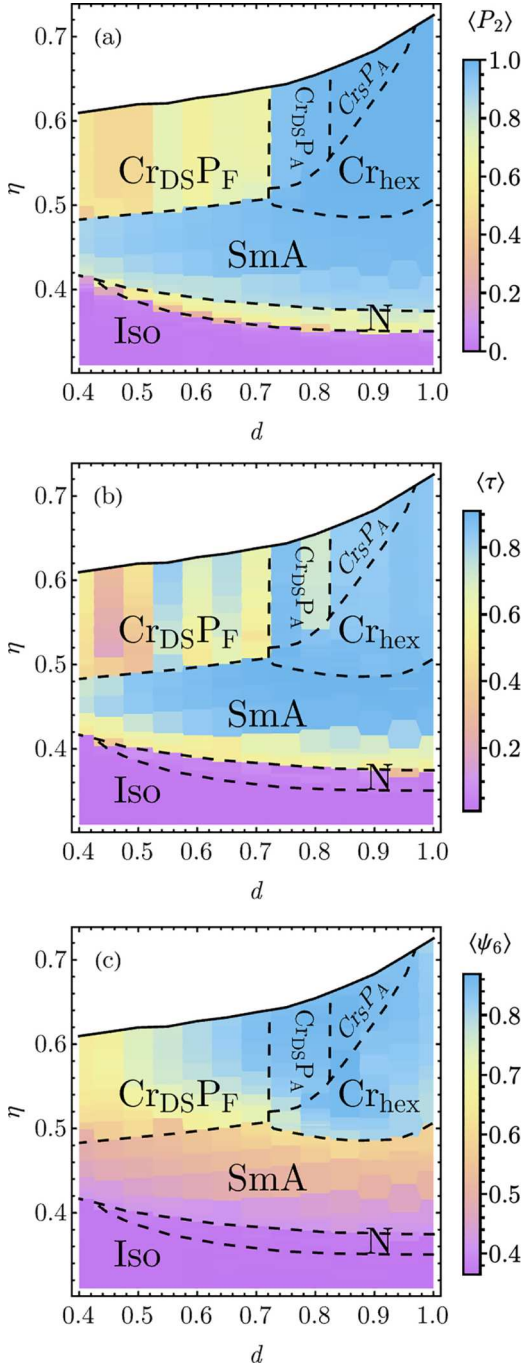


FIG. 3. Ensemble averages of observables as a function of the smallest sphere's diameter d and packing fraction η . (a) Nematic order $\langle P_2 \rangle$, (b) smectic order $\langle \tau \rangle$, and (c) local hexatic order $\langle \psi_6 \rangle$.

inspection of system snapshots. They are thoroughly analyzed in the following sections.

A. Liquid phases

For the lowest packing densities η , the system forms an isotropic liquid phase without any long-range translational or

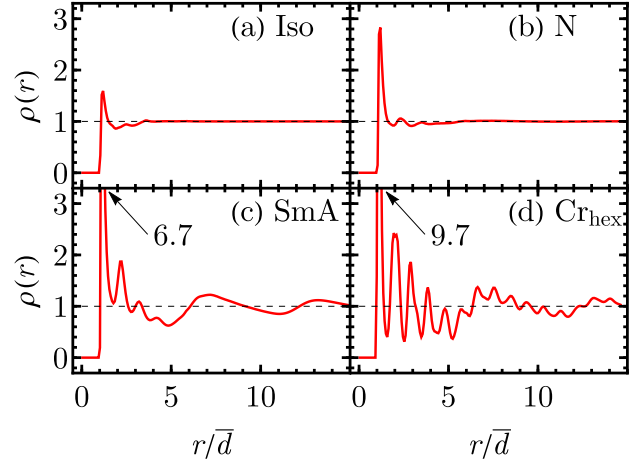


FIG. 4. Radial distribution function $\rho(r)$ for (a) Iso $[(d, \eta) = (0.6, 0.34)]$, (b) N $[(d, \eta) = (0.5, 0.39)]$, (c) SmA $[(d, \eta) = (0.5, 0.46)]$, and (d) Cr_{hex} $[(d, \eta) = (0.95, 0.51)]$ phases. Distance r is scaled by the average diameter of balls in the molecule: $\bar{d} = (d + 1)/2$. Correlation peaks are clipped on panels (c) and (d); however, their values are shown inside the plots.

orientational ordering. An example snapshot of this phase is shown in Fig. 8(a). In this phase, the values of the nematic order parameter $\langle P_2 \rangle$ and smectic order parameter $\langle \tau \rangle$ are close to zero, indicating the absence of alignment or layering. The hexatic order parameter $\langle \psi_6 \rangle$ also has a minimal value (see Fig. 3), indicating a lack of hexagonal arrangement. The radial distribution function [Fig. 4(a)] shows only local correlations, which disappear for distances $r/\bar{d} > 4$, where $\bar{d} = (1 + d)/2$ is the average diameter of balls that build the molecule. The maxima and minima are around integer multiples of $\bar{d}$: $r/\bar{d} = 1, 2, \dots$, which can be attributed to the excluded volume effects.

Upon compression, in the range of $d \in [0.5, 1]$ the nematic phase appears stable [see Fig. 8(b)]. In this phase, the molecules orient, on average, along a preferred direction called the director $\hat{n}$, while maintaining liquidlike positions of their centers of mass. The nematic order parameter $\langle P_2 \rangle$ exhibits a sharp increase at the phase boundary, jumping from 0 to 0.5–0.6 [Fig. 3(a)]. The smectic order parameter $\langle \tau \rangle$ and the hexatic order parameter $\langle \psi_6 \rangle$, however, remain nearly minimal [Figs. 3(b) and 3(c)]. The range of the nematic phase in terms of packing fraction ($\Delta\eta$) is approximately $\Delta\eta \approx 0.03$ for all d , but it drops to zero for the lowest values of d . The Iso-N phase boundary reaches a minimal value of $\eta \approx 0.35$ for the highest value of d and then moves upward towards a triple point $(d, \eta) = (0.5, 0.4)$ as d decreases.

It is expected that as the value of d decreases, the molecules become shorter (less anisotropic). Consequently, a higher pressure is needed to induce ordering in the system. As η increases, the nematic order parameter $\langle P_2 \rangle$ reaches values of 0.6–0.8. These values are relatively high compared to the typical range observed in experiments [0.3, 0.7] [53]. However, they are comparable to values reported in computational studies of other hard-shaped molecules [18, 38, 54].

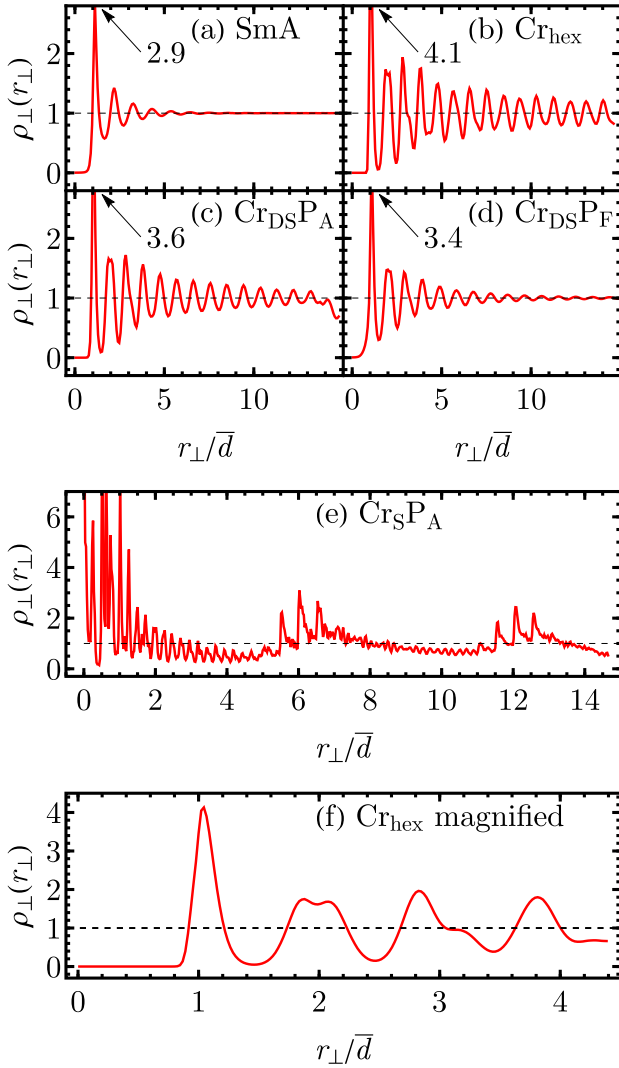


FIG. 5. Layerwise distribution function $\rho_{\perp}(r_{\perp})$ for (a) SmA $[(d, \eta) = (0.5, 0.46)]$, (b) Cr_{hex} $[(d, \eta) = (0.95, 0.51)]$, (c) Cr_{DSPA} $[(d, \eta) = (0.75, 0.52)]$, (d) Cr_{DSPF} $[(d, \eta) = (0.6, 0.51)]$, and (e) Cr_{SPA} $[(d, \eta) = (0.9, 0.68)]$ phases. (f) Magnification of a part of panel (b). Distance $r_{\perp}$ is scaled by the average diameter of balls in the molecule: $\bar{d} = (d + 1)/2$. Correlation peaks are clipped on panels (b), (c), and (d); however, their values are shown inside the plots.

The radial distribution function $\rho(r)$ [Fig. 4(b)] exhibits a series of maxima and minima around $r/\bar{d} = 1, 2, \dots$, which is typical for liquids [42]. However, compared to the Iso phase, the first maximum is more than two times higher, indicating stronger correlations. These correlations diminish at larger distances, for $r/\bar{d} > 6$.

In the ferroelectric nematic (N_F) and splay nematic (N_S) phases, a long-range polarization order is present. Thus, it is imperative to quantify it in our system. Although layers are not present in the nematic phase, it is still possible to compute $S_{\perp}^{110}(r_{\perp})$. The simplest solution would be to project all molecules onto a single plane. However, in order to facilitate capturing local correlations, we divided the box into six iden-

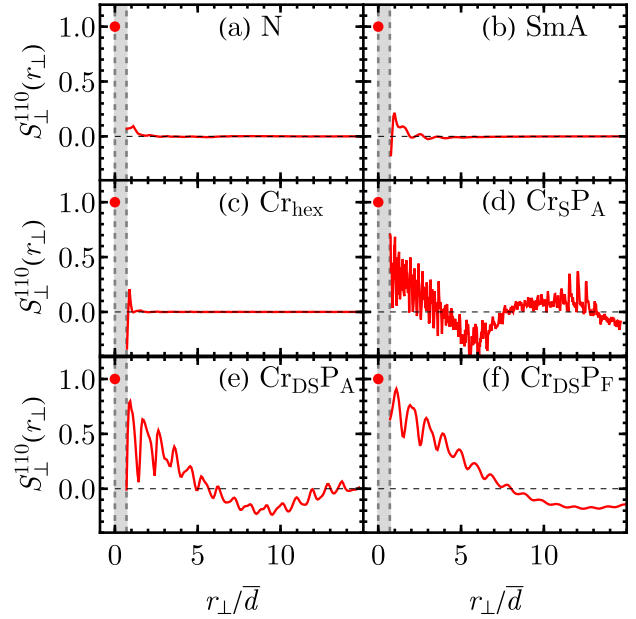


FIG. 6. Layerwise correlation function $S_{\perp}^{110}(r_{\perp})$ for (a) N $[(d, \eta) = (0.5, 0.34)]$, (b) SmA $[(d, \eta) = (0.5, 0.46)]$, (c) Cr_{hex} $[(d, \eta) = (0.95, 0.51)]$, (d) Cr_{SPA} $[(d, \eta) = (0.9, 0.68)]$, (e) Cr_{DSPA} $[(d, \eta) = (0.75, 0.52)]$, and (f) Cr_{DSPF} $[(d, \eta) = (0.6, 0.51)]$ phases. Distance $r_{\perp}$ is scaled by the average diameter of balls in the molecule: $\bar{d} = (d + 1)/2$. Due to excluded volume, there are scarcely any molecules in range $r_{\perp} \in [0, \bar{d}]$; therefore, this area is grayed out.

tical slices (consistent with the number of layers in smectic and crystalline phase) and proceeded to compute $S_{\perp}^{110}(r_{\perp})$ as it would be done for layered structures. The results are presented in Fig. 6(a). It is evident that the polarization correlations are relatively weak and short ranged, vanishing completely for $r_{\perp} > 2\bar{d}$. Similarly, the splay correlations [Fig. 7(a)] also exhibit a local range. The most probable angle in the system is approximately $\theta \approx 25^\circ$, although the maximum has a broad distribution.

The type-A smectic phase (SmA) is formed over the Iso phase for $r \in [0.4, 0.5]$ and over the N phase for $r \in [0.5, 1.0]$. This phase is characterized by a significant jump in the smectic order parameter $\langle \tau \rangle$ [Fig. 3(b)] to around 0.5, indicating the emergence of well-defined layers [as seen in the snapshot from Fig. 8(c)]. The director $\hat{\mathbf{n}}$ is parallel to the smectic wave vector $\mathbf{k}$, indicating the preferred orientation of the molecules within the layers.

In the SmA phase, there is a slight increase in the value of the parameter $\langle \psi_6 \rangle$ compared to the isotropic and nematic phases, ranging from 0.38 to 0.45. In the high packing fraction regime of this phase, $\langle \psi_6 \rangle$ reaches values of 0.6–0.65, indicating some degree of local hexatic ordering within the layers. However, it is important to note that long-range bond order is not present in this phase [55], distinguishing it from other smectic phases such as type-B smectic [56]. The nematic order parameter $\langle P_2 \rangle$ in SmA increases with increasing η , approaching a value close to 1. However, there is no sudden jump in $\langle P_2 \rangle$ at the N-SmA boundary. Similar to the N phase,

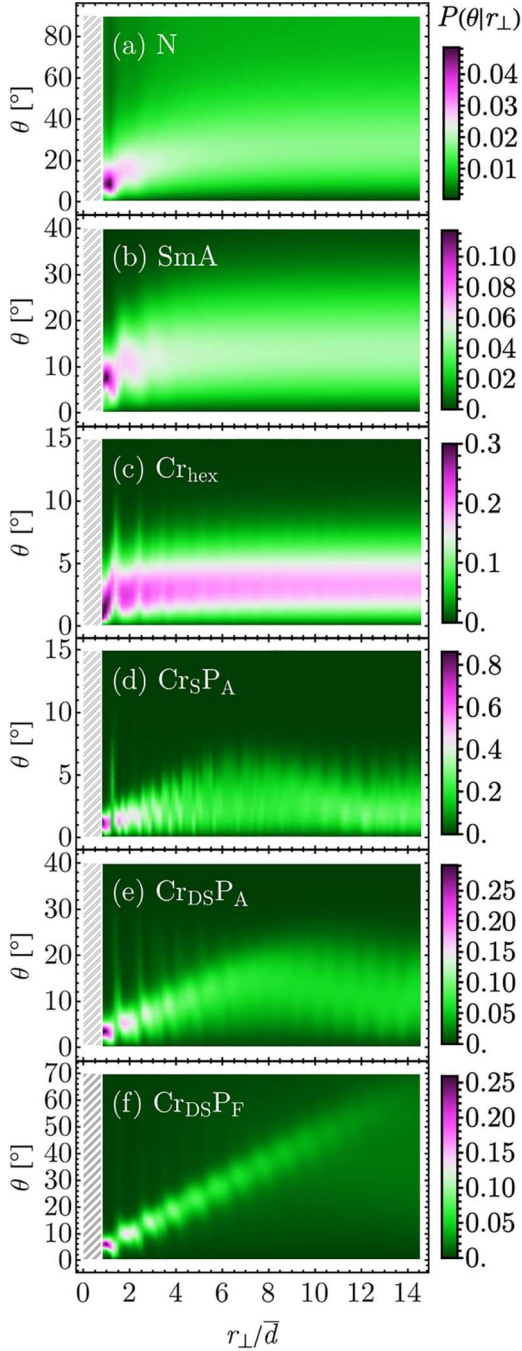


FIG. 7. The conditional probability $P(\theta|r_{\perp})$ for (a) N $[(d, \eta) = (0.5, 0.34)]$, (b) SmA $[(d, \eta) = (0.5, 0.46)]$, (c) Cr_{hex} $[(d, \eta) = (0.95, 0.51)]$, (d) $\text{Cr}_{\text{S}}\text{P}_A$ $[(d, \eta) = (0.9, 0.68)]$ (e) $\text{Cr}_{\text{DS}}\text{P}_A$ $[(d, \eta) = (0.75, 0.52)]$, and (f) $\text{Cr}_{\text{DS}}\text{P}_F$ $[(d, \eta) = (0.6, 0.51)]$ phases.

the boundary moves upward with decreasing d , which can again be explained by a lower anisotropy of the molecules.

The radial distribution function $\rho(r)$ [see Fig. 4(c)] in SmA exhibits a more complex structure compared to the Iso and N phases. It shows two superimposed sequences of minima and maxima. The first sequence, covering the entire range of

$r/\bar{d}$, exhibits maxima at $r/\bar{d} \approx 7$ and 14, corresponding to the distances between the layers. The second sequence has a spacing of approximately $\bar{d}$ and vanishes for $r/\bar{d} > 6$. The first maximum in the second sequence is sharp and has a value of $\rho(r) = 6.7$, corresponding to short-range ordering of molecules within the layers.

The layerwise distribution function $\rho_{\perp}(r_{\perp})$ [Fig. 5(a)] confirms the local translational order within the layers. It shows maxima at $r_{\perp}/\bar{d} = 1, 2, \dots$, indicating correlations between molecules within the same layer. However, these correlations phase out for $r_{\perp}/\bar{d} > 9$, indicating that the translational order is only local within the layers.

The correlation function $S_{\perp}^{110}(r_{\perp})$ [Fig. 6(b)] shows no long-range correlation of molecular polarization vectors in SmA. For $r_{\perp}/\bar{d} \approx 1$ a slight anticorrelation [$S_{\perp}^{110}(r_{\perp}) < 0$] is visible due to entropic reasons, where nearest-neighbor molecules tend to orient in opposite ways to increase packing density. However, these correlations vanish for $r_{\perp}/\bar{d} > 4$. Similarly, the splay correlations [Fig. 7(b)] remain only local within the smectic-A phase. The preferred angle for splay correlations is lower ($\theta \approx 12^\circ$) compared to the N phase, and the spread of angles is also lower, which is consistent with the higher value of the nematic order parameter $\langle P_2 \rangle$ in the smectic phase.

Both sequences of phase transitions displayed by the system, (1) Iso $\leftrightarrow$ N $\leftrightarrow$ SmA and (2) Iso $\leftrightarrow$ SmA, are prominent and well recognized in systems of elongated molecules, both in computational studies [17,18,38,54], and in experiments [57–59], although the second sequence is less common in physical systems.

For asymmetric molecules, modulated and/or polar liquid crystalline phases may form (see the Introduction section). However, in our model, such phases were not observed. The absence of ferroelectric long-range order, even in the metastable regime, is further confirmed by bifurcation analysis using Parsons-Lee density functional theory (see Sec. IV). Two possible reasons for this absence can be considered: the first one is the moderate length of the molecule, which may hinder the formation of long-range ferroelectric-like order, and the second one is the concavities between the beads in the molecular structure. We, however, note that preliminary studies of analogous systems of taper-shaped molecules built of up to 11 beads as well as ones with the smooth, convex surface show no considerable change in the predictions presented by the current study.

B. Crystalline phases

Over $\eta \approx 0.5$, four distinct types of hexagonally ordered solids that retain the SmA layered structure appear.

1. Hexagonal nonpolar crystal Cr_{hex}

For $d \in [0.75, 1.0]$, SmA is adjacent to a hexagonal nonpolar crystal phase denoted Cr_{hex} , whose snapshot is shown in Fig. 9(a). Both $\langle P_2 \rangle$ and $\langle \tau \rangle$ are almost equal to 1 in the entire range, as seen in Figs. 3(a) and 3(b). Additionally, there is a sharp jump in the local hexatic order parameter, as depicted in Fig. 3(c), confirming the presence of a locally hexatic structure within a layer. The long-range translational order becomes apparent when observing the radial and layerwise

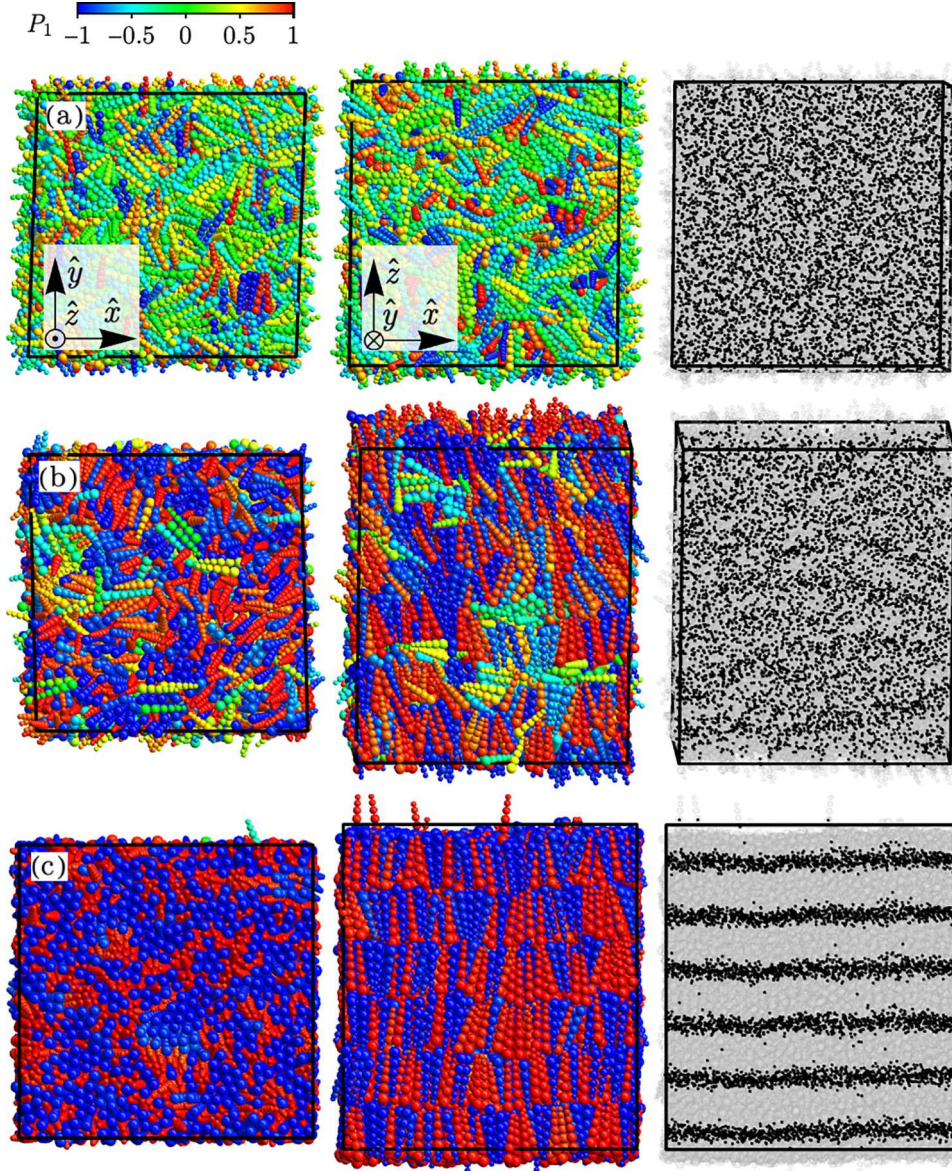


FIG. 8. System snapshots of all liquid phases in the system. Rows correspond to (a) Iso $[(d, \eta) = (0.6, 0.34)]$, (b) N $[(d, \eta) = (0.5, 0.39)]$, and (c) SmA $[(d, \eta) = (0.5, 0.46)]$ phases. The first column presents the top view of the snapshot (xy plane), and the second one the side view (xz) plane in a way that the bottom edge of the top view corresponds to the top edge of the side view. Molecules are color coded according to orientation of their long axis $\hat{\mathbf{a}}_i$ with respect to the global director $\hat{\mathbf{n}}$ as per first-order Legendre polynomial $P_1(\hat{\mathbf{a}}_i \cdot \hat{\mathbf{n}}) = \hat{\mathbf{a}}_i \cdot \hat{\mathbf{n}}$, allowing one to discern opposite polarizations. In the third column midpoints of molecules' lengths are marked as black dots, and the simulation box is oriented in the same way as the second column (side view).

pair distribution functions $\rho(r)$ and $\rho_\perp(r_\perp)$, respectively, as shown in Figs. 4(d) and 5(b). In the case of $\rho(r)$, we observe two sequences of maxima. Similar to SmA, the first sequence with larger spacing corresponds to layering, while the second sequence with a smaller peak-to-peak distance corresponds to in-layer order. However, unlike SmA, the second sequence does not vanish quickly and extends throughout the entire plotted range of $r/\bar{d}$. Similarly, $\rho_\perp(r_\perp)$ also exhibits long-range correlations. Additionally, the structure of the first few peaks of $\rho_\perp(r_\perp)$, as shown in Fig. 5(f), agrees with the one observed for the hexagonal honeycomb lattice (see, e.g., Fig. 3 of

Ref. [60]). The $S_\perp^{110}(r_\perp)$ correlations, as depicted in Fig. 6(c), indicate weak and extremely short-range polarization order, which disappears for $r_\perp/\bar{d} > 2$. A similar observation can be made for the splay correlations shown in Fig. 7(c), where the preferred angle is close to 0° with a very narrow spread. The presence of a series of additional vertical lines is possibly a result of lattice defects.

For $d = 1$, the taper reduces to a well-known linear tangent hard-sphere (LTHS) hexamer. The equilibrium phases in the LTHS model have been studied in Ref. [38]. The ground-state configuration in this case is a close-packed arrangement of

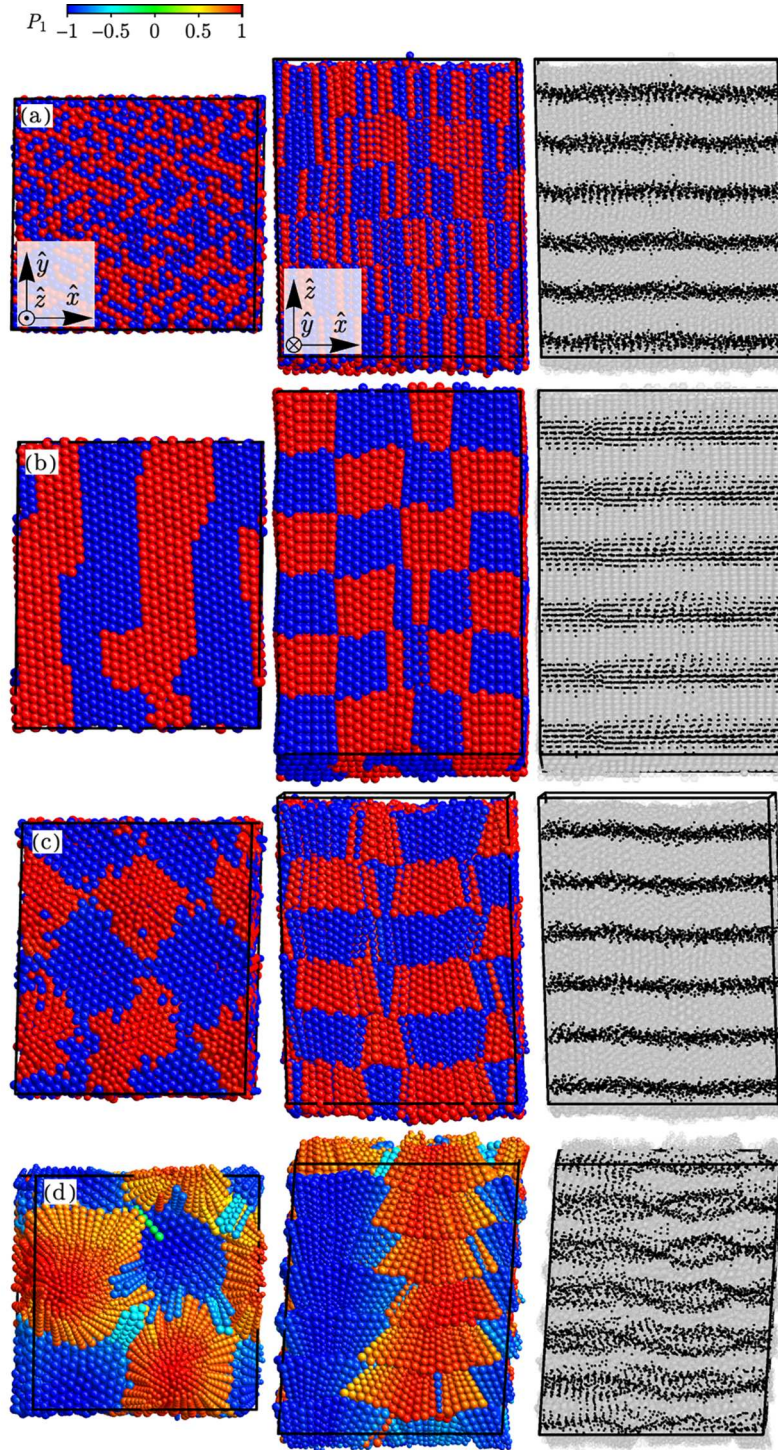


FIG. 9. System snapshots of all crystalline phases in the system. Rows correspond to, respectively, (a) Cr_{hcp} $[(d, \eta) = (0.95, 0.51)]$, (b) Cr_{sPA} $[(d, \eta) = (0.9, 0.68)]$, (c) Cr_{DsPA} $[(d, \eta) = (0.75, 0.52)]$, and (d) Cr_{DsPF} $[(d, \eta) = (0.6, 0.51)]$ phases. Columns' order and color coding are the same as in Fig. 8. From the left: top view, side view, and side view of molecules lengths' midpoints. The average number of molecules in clusters is as follows: (b) ≈ 7 per stripe per XZ section, (c) ≈ 110 per cluster, and (d) ≈ 220 per column per layer.

spheres [61], with a packing fraction of $\eta = \pi/\sqrt{18} \approx 0.74$. In our simulations, we were able to achieve a packing fraction of approximately $\eta \approx 0.73$ upon compression, which is in good agreement with the exact value, taking into account the

presence of a small number of defects in the Monte Carlo configuration. There are various ways to arrange LTHS chains into a close-packed configuration. One obvious choice is to form face-centered cubic (fcc) or hexagonal close-packed

(hcp) layers of molecules with a 30° tilt (e.g., the CP_1 lattice in Ref. [62], also utilized in the previously mentioned Ref. [38]). However, these configurations are unlikely to form during the compression route from SmA layers.

More probable are nontilted variants with a partial hexatic order. We have identified two such structures referred to as fcc_B and hcp_B (see the Appendix). In these structures, six nearest neighbors within a layer form slightly deformed regular hexagons. This deformation is consistent with the values of $\langle\psi_6\rangle$ below 0.8 for $d = 1$, compared to over 0.8 for $d = 0.85$. In the fcc_B and hcp_B lattices, the polymers arrange themselves into infinite columns that can be translated by integer multiples of the diameter $d = 1$ of the monomers. Our results exhibit a slight off-layer spread [observed in the last column of Fig. 9(a)], which also contributes to lowering the value of $\langle\tau\rangle$.

2. Antiferroelectric splay crystal $Cr_S P_A$

When d is decreased and the variation of bead diameters increases, the preference for a closed-packed configuration diminishes, and crystalline analogs of polar blue phases emerge. The first one is visible in a range around $d = 0.85$ – 0.95 (see Fig. 2). The corresponding snapshot is presented in Fig. 9(b). As clearly visible in the snapshot, within each layer, clusters with macroscopic polarization spontaneously emerge and arrange themselves in a striped metastructure. Adjacent clusters exhibit opposite polarization and are separated by planar defects in the polarization field.

Within a cluster, the molecules have a long-range translational order, which is indicated by the correlation function $\rho_\perp(r_\perp)$ [Fig. 5(e)] and they form a hexagonal structure, reflected in a high value of $\langle\psi_6\rangle$ [Fig. 3(c)]. The density correlations exhibit a complex structure. First, there is a series of wide maxima and minima separated by $\Delta r_\perp \approx 6\bar{d}$, which corresponds to the width of the stripes. Around these wide maxima, there are three or four sharper ones separated by $\Delta r_\perp \approx \bar{d}$, representing correlations between particular rows of shapes across the stripes. Additionally, numerous small maxima represent correlations between individual beads in a highly regular lattice. However, this phase appears only for very high values of η close to the maximal packing. The macroscopic polarization of the cluster is confirmed by $S_\perp^{110}(r_\perp)$ correlations [see Fig. 6(d)]. Similarly, for $\rho_\perp(r_\perp)$, we observe minima and maxima, but with a twofold smaller separation, as the adjacent stripes have opposite polarizations. Furthermore, there is a similar series of additional maxima as observed in $\rho_\perp(r_\perp)$.

The nematic order $\langle P_2 \rangle$ remains above 0.8 but is slightly lower than for Cr_{hex} . This can be explained by the observation that clusters exhibit a splay modulation in the polarization field. Specifically, the polarization is parallel to the director in the middle of the stripe and gradually leans when one moves towards the boundary. However, the preferred direction does not change along the length of a stripe. This observation is supported by the $P(\theta|r_\perp)$ histogram [Fig. 7(d)], where, for the first time, a linear growth of the preferred angle θ with $r_\perp$ is observed until $r_\perp \approx 7\bar{d}$. After this point, a linear decline follows. The ascending part of the histogram corresponds

to correlations within a single stripe, while the falling part corresponds to correlations between adjacent stripes.

The entropically promoted pure splay, inherently related to the shape of the taper, cannot be extended globally without introducing energetically expensive defects. The observed two-dimensional splay modulation serves as a solution to this difficulty (frustration), enabling a more efficient filling of space. Notably, the pattern of clusters in adjacent layers continues, but their polarization always has an opposite sign. The same sign reversal applies to the direction of splay modulation. Consequently, the stripes (y -axis columns) are arranged in a two-dimensional checkerboard pattern. The largest and smallest balls that form the molecules create hexagonal lattices with different lattice constants. The polarization switch in a neighboring layer facilitates a more compatible arrangement of adjacent layers.

The compatibility of lattice constants between adjacent beads can also be invoked to explain why molecules splay instead of forming an antiferroelectric interdigitated lattice, as observed in previous studies of pearlike shapes. When two adjacent tapers are antiparallel, the beads in contact have different radii, resulting in suboptimal local packing. In contrast, when the molecules are parallel, equally sized beads from adjacent molecules can be tangent, allowing them to form a nearly optimal local configuration.

To capture the most important properties of the structure, we refer to it as the *antiferroelectric splay crystal*, denoted as $Cr_S P_A$. The term *antiferroelectric* refers to the opposite polarization of the clusters in adjacent layers. It is worth noting that the $Cr_S P_A$ phase emerges even when the value of d is close to 1. However, the phase boundary significantly increases as d grows. This behavior can be attributed to the requirement of higher densities to induce polar order when the gradient of ball diameters is smaller. In the entire range, the system first crystallizes into the Cr_{hex} structure, followed by a transition to the $Cr_S P_A$ phase. Therefore, there is no direct SmA- $Cr_S P_A$ phase transition present.

3. Antiferroelectric double-splay crystal $Cr_{DS} P_A$

Above Cr_{hex} , another polar phase is observed for $0.75 \leq d \leq 0.8$. The corresponding snapshot is shown in Fig. 9(c). In this phase, polarization clusters form again, but they arrange themselves within a layer in a checkerboard pattern instead of stripes. Each square domain is surrounded by four domains with opposite polarization. When moving to an adjacent layer, the polarizations of the clusters flip, similar to $Cr_S P_A$. This indicates that the checkerboard pattern is actually three dimensional.

The splay pattern also changes in this phase. It becomes three dimensional, where the direction of the splay vector $\hat{n}(\nabla \cdot \hat{n})$ is correlated with the polarization field. The molecules within the cluster are parallel to the z axis in the middle and gradually lean as the distance from the center increases. This structure is referred to as the *antiferroelectric double-splay crystal* ($Cr_{DS} P_A$). Importantly, the magnitude of the splay vector in the double-splay structure is higher compared to that in the single splay structure (assuming the same maximal curvature). This higher splay deformation is facilitated by molecules with smaller values of d , which

promotes a stronger modulation of the director field ultimately leading to the formation of the checkerboard pattern observed in $\text{Cr}_{\text{DS}}\text{P}_\text{A}$. It is also reflected in a slightly lower value of $\langle P_2 \rangle$ compared to $\text{Cr}_\text{S}\text{P}_\text{A}$.

In the $\text{Cr}_{\text{DS}}\text{P}_\text{A}$ phase, the transversal density correlation $\rho_\perp(r_\perp)$ [Fig. 5(c)] exhibits a similar behavior as in the Cr_{hex} [Fig. 5(b)], but with higher damping. The angle histogram $P(\theta|r_\perp)$ [Fig. 7(e)] in the $\text{Cr}_{\text{DS}}\text{P}_\text{A}$ phase is also similar to that in the $\text{Cr}_\text{S}\text{P}_\text{A}$ phase [Fig. 7(d)], but with larger preferred angles. Again, the difference is a result of stronger splay deformation in $\text{Cr}_{\text{DS}}\text{P}_\text{A}$ compared to $\text{Cr}_\text{S}\text{P}_\text{A}$. Regarding the polarization correlation function $S_\perp^{110}(r_\perp)$ [Fig. 6(e)], it shows positive correlations up to $r_\perp \approx 6.5\bar{d}$, and then negative correlations up to $r_\perp \approx 13\bar{d}$. This behavior is consistent with the snapshot in Fig. 9(c), where the cluster radius is estimated to be approximately six to seven times the average diameter of balls that build the molecule ($6\bar{d}$ – $7\bar{d}$).

It is important to note that for a moderate number of molecules used in our study, the cluster radius may not be able to relax to its equilibrium value. The structure must adhere to periodic boundary conditions, which necessitates a single layer enclosing an even number of clusters. This requirement quantifies the surface area of the simulation box base. Simultaneously, the box height is constrained by the layer's width, and its volume is determined by the packing fraction. These parameters cannot be relaxed independently, even in a general triclinic simulation box. Consequently, the cluster radius is subject to systematic error. For a system in Fig. 9(c), the box accommodates eight clusters with a radius of approximately $6.5\bar{d}$. The two closest values are approximately $5.6\bar{d}$ and $7.3\bar{d}$, corresponding to six and ten clusters, respectively. Thus, the estimated uncertainty range of the radius can be approximated as $[(6.5 + 5.6)\bar{d}/2, (7.3 + 6.5)\bar{d}/2] \approx [6.0\bar{d}, 6.9\bar{d}]$. It is important to bear in mind that the slight nonequilibrium cluster radius can introduce frustration, potentially affecting other characteristic lengths, and consequently altering the uncertainty range. Finally, it should be noted that this issue did not arise in the two-dimensional $\text{Cr}_\text{S}\text{P}_\text{A}$ metastructure, where all structural dimensions could be relaxed independently.

4. Ferroelectric double-splay crystal $\text{Cr}_{\text{DS}}\text{P}_\text{F}$

For $d < 0.75$, the third frustrated polar structure, called the *ferroelectric double-splay crystal* ($\text{Cr}_{\text{DS}}\text{P}_\text{F}$), is formed directly above the SmA phase. Similar to $\text{Cr}_{\text{DS}}\text{P}_\text{A}$, the $\text{Cr}_{\text{DS}}\text{P}_\text{F}$ phase also exhibits the formation of polar clusters arranged in a checkerboard pattern [cf. Fig. 9(d)]. However, unlike $\text{Cr}_{\text{DS}}\text{P}_\text{A}$, where the clusters alternate between neighboring layers, in $\text{Cr}_{\text{DS}}\text{P}_\text{F}$ the clusters form vertical columns along the z axis that extend throughout the entire height of the simulation box.

The formation of these columns is accompanied by the bending of layers, as seen in the second and third panels of Fig. 9(d). Additionally, the decrease in the smectic order parameter $\langle \tau \rangle$ to the range 0.4–0.7 further indicates a curved layer structure. These curved layers cause the hexatic arrangement to deform when orthogonally projected, resulting in a lower hexatic order parameter $\langle \psi_6 \rangle$ in the range 0.65–0.75. The weaker nematic order $\langle P_2 \rangle$ in the range 0.5–0.8 is also consistent with the observed curved layers, which induce significant splay modulation.

Why is the $\text{Cr}_{\text{DS}}\text{P}_\text{F}$ structure stabilized for $d < 0.75$? For a simple explanation, please note that in $\text{Cr}_\text{S}\text{P}_\text{A}$ and $\text{Cr}_{\text{DS}}\text{P}_\text{A}$ the opposite interlayer polarization allows for the adjacency of compatible hexagonal bead lattices. However, this arrangement enforces flat layers, which becomes inefficient for smaller values of d . An efficient packing arrangement that leads to higher packing densities involves clusters that resemble fragments of a spherical shell. Achieving such an arrangement would require a ferroelectric alignment in the direction of the vector $\mathbf{k}$ to match the signs of curvatures. Interestingly, this is precisely what happens in the transition from $\text{Cr}_{\text{DS}}\text{P}_\text{A}$ to $\text{Cr}_{\text{DS}}\text{P}_\text{F}$. The formation of columns in $\text{Cr}_{\text{DS}}\text{P}_\text{F}$ allows for layer bending and the emergence of a mutually coupled ferroelectric arrangement in this phase. Although this ordering sacrifices the compatibility of the lattice constants of the beads, the packing microstructure remains similar to $\text{Cr}_{\text{DS}}\text{P}_\text{A}$.

There are long-range correlations observed in the transversal density correlation $\rho_\perp(r_\perp)$ [Fig. 5(d)], which, however, vanish faster than for $\text{Cr}_{\text{DS}}\text{P}_\text{A}$ or Cr_{hex} . This can be attributed to more irregular domain walls, which weaken the correlations between adjacent clusters. The polarization correlation function $S_\perp^{110}(r_\perp)$ [Fig. 6(f)] in $\text{Cr}_{\text{DS}}\text{P}_\text{F}$ is similar to that in $\text{Cr}_{\text{DS}}\text{P}_\text{A}$, and the cluster radius estimated at seven to eight molecule diameters agrees with a visual inspection of Fig. 9(d). The preferred angles on the angle histogram $P(\theta|r_\perp)$ [Fig. 7(f)] grow linearly with $r_\perp$, confirming the presence of long-range splay correlations. However, unlike in Figs. 7(d) and 7(e), a linear descent in the angle histogram is not observed in $\text{Cr}_{\text{DS}}\text{P}_\text{F}$.

Finally, with decreasing d the variation of ball diameters grows larger, which hinders the optimal filling of the space. As a result, the estimated maximal packing fraction η (see black solid line in Fig. 2) falls monotonically with d , reaching $\eta \approx 0.61$ for $d = 0.4$.

IV. DENSITY FUNCTIONAL ANALYSIS OF LIQUID CRYSTALLINE ORDER

Simulations show that the shape-induced splay deformations in the system of taper-shaped hard molecules can lead to unusually complex long-range orientational ordering in crystalline phases. What is somewhat unexpected is that the observed long-range orientational order in the liquid crystalline phases is not affected much. That is, only the ordinary uniaxial nematic and smectic-A phases are found at equilibrium. The question remains of whether liquid crystalline phases of non-trivial orientational ordering, such as e.g. ferroelectric nematic, ferroelectric smectic A, antiferroelectric smectic A, splay nematic or splay smectic, can form subject to purely steric interactions. Although we did not observe these in simulations as equilibrium states, it is imperative to assess whether such polar liquids are formed at least in a metastable regime. The simplest way to approach this issue is to perform density functional bifurcation analysis, in which the form of stable or metastable states can be selected at the start. In the following, we concentrate on the potential (meta)stability of ferroelectric nematic (N_F), smectic-A (SmA), and (anti)ferroelectric smectic-A (SmA_AF) phases using the second-virial density functional theory corrected by

the Parsons-Lee term (DFTPL) [63–65]. We will seek to gain a better understanding of the ability of taper-shaped molecules to form liquid phases with polar order. The study of the N-SmA bifurcation here serves as a reference.

The use of the DFTPL approach proved especially useful in the analysis of (meta)stable structures for hard molecules of complex shapes (see, e.g., Ref. [16]). We start with a brief summary of DFTPL for hard uniaxial molecules. More details can be found, e.g., in Refs. [16,66,67]. According to this theory, the Helmholtz free energy $\mathcal{F}$ of a system of N molecules in volume V at temperature T is a functional of the single-molecule probability density distribution function $P(X_i)$, where $X_i \equiv \{\mathbf{x}_i, \hat{\mathbf{a}}_i\}$ represents the position and orientation of the i th molecule. The distribution $P(X_i)$ is normalized so that

$$\text{Tr}_{(X_i)} P(X_i) = 1, \quad \text{Tr}_{(X_i)} = \int_V d^3\mathbf{r}_i \int d^2\hat{\mathbf{a}}. \quad (10)$$

After disregarding terms that can be made independent of P , the relevant part of the free energy per molecule for hard uniaxial molecules of arbitrary shape can be written as

$$f(P) \equiv \frac{\mathcal{F}[P]}{Nk_B T} = \text{Tr}_{(X)} [P(X) \ln P(X)] + C(\eta) \frac{\bar{\rho}}{2} \text{Tr}_{(X)} [P(X) H_{\text{eff}}(X, [P])] + \dots, \quad (11)$$

where $\bar{\rho} = \frac{N}{V}$ is the average density. H_{eff} is the effective excluded volume averaged over the probability distribution of molecule “2” ($X \equiv X_1$):

$$H_{\text{eff}}(X_1, [P]) = V \text{Tr}_{(X_2)} \{ \Theta[\xi(X_1, X_2) - r_{12}] P(X_2) \}, \quad (12)$$

where $\xi(\cdot)$ is the contact distance between two molecules, $\Theta(\cdot)$ is the Heaviside Θ function, and k_B is the Boltzmann constant. The factor $C(\eta) = (1/4) \frac{4-3\eta}{(1-\eta)^2}$ renormalizes the second-order virial expansion [63] to take into account the higher-order terms of the expansion [64,65]. Finally, r_{12} is the distance between two molecules, $\eta = \frac{v_{\text{mol}} N}{V} = v_{\text{mol}} \bar{\rho}$ is the packing fraction, and v_{mol} is the volume of a molecule.

The equilibrium states correspond to the minimum of the free energy functional, Eq. (11), with respect to $P(X)$, subject to the normalization condition, Eq. (10). The procedure is equivalent to solving the self-consistent integral equation for the stationary distributions $P_s(X)$:

$$P_s(X) = Z^{-1} \exp[-\bar{\rho} C(\eta) H_{\text{eff}}(X, [P_s])], \quad (13)$$

where

$$Z = \text{Tr}_{(X)} \exp[-\bar{\rho} C(\eta) H_{\text{eff}}(X, [P_s])] \quad (14)$$

and selecting the solution that minimizes the free energy (11) for a given set of control parameters. In general, for taper-shaped molecules, it is important to know whether they can stabilize states with some kind of polar order, such as polar nematics or smectics. The effective method for exploring this problem is the bifurcation analysis of Eq. (13) about the reference state, usually the isotropic or uniaxial nematic phase. Since tapers orient their steric dipole, on average, along the director $\hat{\mathbf{n}}(\mathbf{r})$, different local polar order of the predefined polarization profile $\hat{\mathbf{p}}(\mathbf{r})$ ($|\hat{\mathbf{p}}(\mathbf{r})| = 1$, $\hat{\mathbf{p}}(\mathbf{r}) = \pm \hat{\mathbf{n}}(\mathbf{r})$) can be tested against the instability of the reference state.

Here, we focus on bifurcation studies from the reference uniaxial nematic phase. As simulations show, the nematic order is high in both the uniaxial nematic and at the transition from the uniaxial nematic to higher-ordered phases (see Fig. 2), so we can further simplify the analysis by assuming that the orientational order is saturated. Consequently, the orientational degrees of freedom of the i th polar molecule can be described by a discrete pseudospin variable, $s_i = \pm 1$. It tells whether the steric molecular dipole is parallel ($s_i = 1$) or antiparallel ($s_i = -1$) to the preferred local orientational ordering, which is assumed to be positionally independent:

$$\mathbf{a}_i = s_i \hat{\mathbf{p}}. \quad (15)$$

In this case, the integration of orientational degrees of freedom is reduced to the sum over $s_i = \pm 1$, which means that

$$\begin{aligned} \text{Tr}_{(X_i)} [\dots] &= \text{Tr}_{(\mathbf{r}_i, s_i)} [\dots] \equiv \text{Tr}_{(x_i, y_i, z_i, s_i)} [\dots] \\ &= \int_V d^3\mathbf{r}_i \sum_{s_i = \pm 1} (\dots). \end{aligned} \quad (16)$$

A more complex case of the nematic splay and smectic splay is left for an in-depth discussion elsewhere.

In practical calculations, we model the stationary distribution function $P_s \equiv P(\mathbf{r}, s) \equiv P(z, s)$ by expanding this to leading order in order parameters that describe the structures of interest. By limiting to nematic and smectic polar orderings of the constant $\hat{\mathbf{p}}$ (parallel to the z axis), this gives

$$\begin{aligned} P(z, s) &= \frac{1}{V} \left[\frac{1}{2} + \frac{1}{2} \langle s \rangle s + \langle \cos \rangle \cos \left(\frac{2\pi z}{d'} \right) \right. \\ &\quad + \langle \sin \rangle \sin \left(\frac{2\pi z}{d'} \right) + \langle s \cos \rangle s \cos \left(\frac{2\pi z}{d''} \right) \\ &\quad \left. + \langle s \sin \rangle s \sin \left(\frac{2\pi z}{d''} \right) + \dots \right], \end{aligned} \quad (17)$$

where

$$\begin{aligned} &\{ \langle s \rangle, \langle \cos \rangle, \dots, \langle s \sin \rangle \} \\ &= \text{Tr}_{(\mathbf{r}_i, s_i)} P(z, s) \left\{ s, \cos \left(\frac{2\pi z}{d'} \right), \dots, s \sin \left(\frac{2\pi z}{d''} \right) \right\} \end{aligned} \quad (18)$$

are the order parameters and where the length of the box ($V^{\frac{1}{3}}$) is assumed to be a multiple of the smectic periods d' and d'' .

Note that in expansion, Eq. (17), the order parameter $\langle s \rangle$ represents the long-range polar order of the molecules in the nematic, smectic, and crystalline phases, while $\langle s \rangle \hat{\mathbf{p}}$ is the average polarization. In the case of SmA with density modulation along the z axis of the laboratory frame, only the order parameter $\langle \cos \rangle$ is not zero while d' is the period of the structure. This phase is always stable in simulations and will therefore serve as a test for bifurcation theory. The remaining order parameters can be combined to form antiferroelectric smectic phases, but detailed predictions depend on the solutions of Eq. (13).

The calculations can now proceed by pointing out that the order parameters are small near the bifurcation point. This

enables us to linearize Eq. (13) for a very small nonzero value of $\delta P(z, s)$, where $\delta P(z, s) = P(z, s) - P_0$; $P_0 = \frac{1}{2V}$ takes into account the probability distribution of the ideally oriented uniaxial nematic phase. The resulting linear homogeneous equation for $\delta P(z, s)$ is given by

$$\delta P(z_1, s_1) = -\eta C(\eta) \left(\frac{1}{2v_{\text{mol}}} \right) \text{Tr}_{(z, s_2)} [\Theta(z, s_1, s_2) \delta P(z + z_1, s_2)]. \quad (19)$$

Here $\Theta(z, s_1, s_2) = \text{Tr}_{(x_{12}, y_{12})} \Theta[\xi(\mathbf{r}_{12}, s_1, s_2) - r_{12}]$ ($z \equiv z_{12}$), and v_{mol} is the volume of the molecule.

Before identifying the phases that can bifurcate from N , we observe that the excluded interval $\Theta(z, s_1, s_2)$ has a particularly simple form in relation to the variables $\{s_1, s_2\}$. Specifically, observing the symmetry of $\Theta(z, s_1, s_2)$, $\Theta(z, -1, 1) = \Theta(-z, 1, -1)$ and $\Theta(z, -1, -1) = \Theta(z, 1, 1) = \Theta(-z, 1, 1)$, we can replace $\Theta(z, s_1, s_2)$ with the sum

$$\Theta(z, s_1, s_2) = \Theta_0(z) + s_1 s_2 \Theta_1(z) + (s_1 - s_2) \Theta_2(z), \quad (20)$$

where

$$\Theta_0(z) = \Theta_0(-z) = \frac{1}{4} [2 \Theta(z, 1, 1) + \Theta(z, 1, -1) + \Theta(-z, 1, -1)], \quad (21)$$

$$\Theta_1(z) = \Theta_1(-z) = \frac{1}{4} [2 \Theta(z, 1, 1) - \Theta(z, 1, -1) - \Theta(-z, 1, -1)], \quad (22)$$

and where

$$4\Theta_2(z) = -4\Theta_2(-z) = \Theta(z, 1, -1) - \Theta(-z, 1, -1). \quad (23)$$

It should be noted that the term proportional to $(s_1 + s_2)$ disappears due to the symmetries mentioned above of $\Theta(z, s_1, s_2)$.

Now, the homogeneous Eq. (19) can be solved for $\delta P(z_1, s_1)$, and the solutions are parametrized by the corresponding packing fraction $\eta = \eta_b$. More specifically, for $P(z, s)$ given by Eq. (17), Eq. (19) becomes reduced to a set of homogeneous equations for the order parameters. They are given by

$$\langle s \rangle = \langle s \rangle \psi(\eta_b) \Theta_{1,s}, \quad (24)$$

$$\begin{aligned} \begin{pmatrix} \langle \cos \rangle \\ \langle s \sin \rangle \end{pmatrix} &= \psi(\eta_b) \begin{pmatrix} \Theta_{0,c}(d') & -\Theta_{2,s}(d'') \delta_{d',d''} \\ -\Theta_{2,s}(d'') \delta_{d',d''} & \Theta_{1,c}(d'') \end{pmatrix} \begin{pmatrix} \langle \cos \rangle \\ \langle s \sin \rangle \end{pmatrix}, \\ \begin{pmatrix} \langle \sin \rangle \\ \langle s \cos \rangle \end{pmatrix} &= \psi(\eta_b) \begin{pmatrix} \Theta_{0,c}(d') & \Theta_{2,s}(d'') \delta_{d',d''} \\ \Theta_{2,s}(d'') \delta_{d',d''} & \Theta_{1,c}(d'') \end{pmatrix} \begin{pmatrix} \langle \sin \rangle \\ \langle s \cos \rangle \end{pmatrix}, \end{aligned} \quad (25)$$

where

$$\begin{aligned} \Theta_{1,s} &= \int_{-l}^l \Theta_1(z) dz, \\ \Theta_{0,c}(d') &= \int_{-l}^l \Theta_0(z) \cos\left(\frac{2\pi z}{d'}\right) dz, \\ \Theta_{2,s}(d') &= \int_{-l}^l \Theta_2(z) \sin\left(\frac{2\pi z}{d'}\right) dz, \\ \Theta_{1,c}(d'') &= \int_{-l}^l \Theta_1(z) \cos\left(\frac{2\pi z}{d''}\right) dz, \end{aligned} \quad (26)$$

and where $\psi = -\frac{2\pi}{v_{\text{mol}}} \eta C(\eta)$; l is the molecular length. We should add that with Wolfram *Mathematica* the formulas for the coefficients $\Theta_{\alpha,\beta}$ can be found exactly for rational diameters of the spheres.

A priori one expects four types of bifurcating states from Eq. (25). The first is the ferroelectric phase (F), where only $\langle s \rangle$ becomes nonzero at η_b . Due to the symmetry of the reference state P_0 and of the excluded interval, Eq. (20), first-order bifurcation analysis does not lead to a coupling between $\langle s \rangle$ and the smectic or crystalline order. Thus, if any F results from Eq. (25), it cannot be fully identified and can actually correspond to a ferroelectric order of a nematic, smectic, or

crystal phase. To resolve which of the cases applies, a higher-order bifurcation analysis is needed in this case. For $d' \neq d''$ we expect classical smectic A (SmA) phase with nonzero $\langle \cos \rangle$ (equivalently $\langle \sin \rangle \neq 0$) and antiferroelectric smectic A (SmA_{AF}) phase where $\langle s \cos \rangle \neq 0$ (equivalently $\langle s \sin \rangle \neq 0$). The final possibility is where $d' = d''$. In this case, we expect the SmA_d phase, where $\langle \cos \rangle \neq 0$ and $\langle s \sin \rangle \neq 0$, (equivalently $\langle \sin \rangle \neq 0$ and $\langle s \cos \rangle \neq 0$). The phase would be similar to SmA , but with d' incommensurate with l . As two order parameters condense at the bifurcation to SmA_d the corresponding phase transition should generally be of first order.

The structure to stabilize as a result of the phase transition from uniaxial nematic is usually (but not always) the one that leads to the minimum value of η_b . In the case of smectics, the bifurcation packing fraction η_b also depends on d' , which requires additional minimization of η_b with respect to the smectic period. The hierarchy of η_b s gives an idea of possible (meta)stable states that the model can predict.

We begin our detailed analysis by determining whether any type of long-range polar order can occur in our model. The solution $\langle s \rangle \neq 0$ bifurcates from N at η_b satisfying the equation [see Eq. (24)]

$$1 = \psi(\eta_b) \Theta_{1,s}. \quad (27)$$

Only the solution with $\eta_b > 0$, where η_b is smaller than the maximal packing fraction, corresponds to a physically acceptable ferroelectric state. Clearly, it satisfies the integral equation (13) for $\eta > \eta_b$. Note that for $\Theta_{1,s} > 0$ no physical solution of Eq. (27) for η_b exists. In this case, the excluded volume of the parallel arrangement of the steric dipoles prevails over that of the antiferroelectric one, suggesting that the preferred local ordering should be of an antiferroelectric type. The calculations reveal that for all d parameters studied, the bifurcating packing fraction is always negative ($\eta_b < 0$), which means that the ferroelectric polar order is globally unstable at the expense of some kind of antiferroelectric ordering. Interestingly, the same conclusions can be drawn for model molecules composed of one sphere of diameter 1 and five spheres with their diameter chosen at random between 1 and 0.4. We have checked this for a sample of about 10 000 different molecules. Overall, these results suggest that, within the assumptions and simplifications adopted, the density functional theory does not predict the existence of global polar ordering in the hard model systems built out of six spheres.

A similar analysis can be performed to study the bifurcation to SmA and SmA_{AF}. Here, the bifurcation equations ($d' \neq d''$), analogous to Eq. (27), are given by

$$1 = \psi(\eta_b) \Theta_{0,c}(d') \quad \text{for N-SmA}, \quad (28)$$

$$1 = \psi(\eta_b) \Theta_{1,c}(d'') \quad \text{for N-SmA}_{AF}. \quad (29)$$

A more complex case of SmA_d ($d' = d''$) requires diagonalization of the symmetric 2×2 matrix

$$\begin{pmatrix} \Theta_{0,c}(d') & \Theta_{2,s}(d') \\ \Theta_{2,s}(d') & \Theta_{1,c}(d') \end{pmatrix}. \quad (30)$$

It allows us to reduce the matrix equations in Eq. (25) to independent linear equations. For example, taking the first of Eqs. (25) we obtain two independent linear relations similar to Eq. (24), where $\Theta_{1,s}$ is replaced by one of the eigenvalues of the matrix, Eq. (30), and $\langle s \rangle$ by a linear combination of order parameters, $\langle \cos \rangle + \frac{o_{12}}{o_{11}} \langle s \sin \rangle$; o_{ij} s are elements of the orthogonal matrix $\mathbf{o}$ that brings Eq. (30) into the diagonal form. By inspecting Eqs. (25) and (30) we find that in our case the corresponding bifurcation equation along with the bifurcating state becomes

$$\frac{2}{\psi(\eta_b)} = \Theta_{0,c} + \Theta_{1,c} - \sqrt{4\Theta_{2,s}^2 + (\Theta_{0,c} - \Theta_{1,c})^2} \quad (31)$$

$$\frac{\delta P(z, s)}{\varepsilon} = \langle \cos \rangle + \frac{2\Theta_{2,s}}{\Theta_{1,c} - \Theta_{0,c} + \sqrt{4\Theta_{2,s}^2 + (\Theta_{0,c} - \Theta_{1,c})^2}} \langle s \sin \rangle, \quad (32)$$

where ε is an arbitrary parameter. As previously, the physical solution is one that leads to a minimum of $\eta_b > 0$ with respect to d' .

In Fig. 10 shown are η_b s found by numerically solving Eqs. (28), (29), and (31). Out of the assumed model structures, the one that bifurcates first is SmA_d (continuous orange line in Fig. 10). It differs from SmA (black line in Fig. 10), characterized by $\langle \cos \rangle$, by the presence of the extra term $\frac{o_{12}}{o_{11}} \langle s \sin \rangle$ that accounts for the polarization wave. However, the relative importance of this last term is of the order of 1% of the

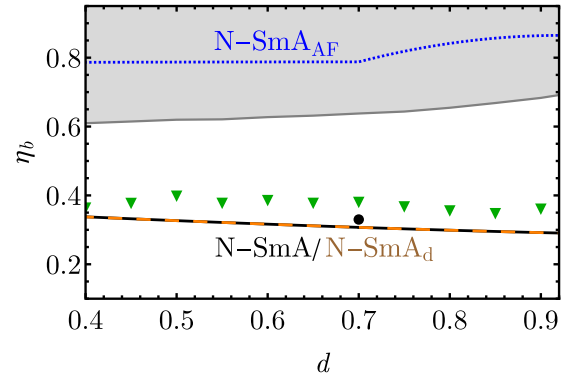


FIG. 10. Bifurcations from ideally oriented nematic phase. The black and orange dashed line denotes two practically overlapping N-SmA and N-SmA_d bifurcation lines, the blue dotted line is the N-SmA_{AF} bifurcation line, and the gray area is an inaccessible region of packing fractions above the optimal packing. Moreover, a black point is the N-SmA transition packing fraction $\eta \approx 0.33$ for $d = 0.7$ obtained from numerical simulation with axis-aligned molecules, while green triangles are N-SmA transition packing fractions from simulations without restricting molecule orientations (cf. Fig. 2).

leading smectic term. The reason for detecting only N-SmA in simulations is probably the nature of the N-SmA_d transition, which should generally be first order due to the simultaneous condensation of two order parameters, unlike N-SmA. When comparing the simulation results with the N-SmA bifurcation, we find that the packing fraction of the bifurcation analysis is always lower than predicted by the simulations. This is due to the underestimation of the orientational entropy by the ideal nematic order, as opposed to the full spectrum of orientational degrees of freedom present in simulations. However, if an ideal nematic order is also assumed in the simulations, a very good agreement between simulation and theory for N-SmA is obtained (black dot shown in Fig. 10). A good agreement is obtained from simulations without restricting molecule orientations (green triangles shown in Fig. 10). A similar analysis for N-SmA_{AF} shows that η_b is generally of the order of 0.8, which exceeds the physically accessible packing fractions for our systems.

V. SUMMARY AND FINAL COMMENTS

One of the most significant discoveries in the field of liquid crystals in recent years is the identification of the ferroelectric nematic phase (N_F) and the nematic phase with periodic long-range splay order (N_S). These phases were initially observed in the RM734 molecular system. While several systems known to exhibit stable polar nematic phases already exist, the key features of molecular interactions responsible for their stability are still under intensive study. Based on observations of molecular self-organization in the RM734 system, two factors appear to play a crucial role in stabilizing these phases: the conelike symmetry of the elongated molecule and the notably large net axial dipole moment of the molecule, exceeding 10 Debye units.

This research represents a systematic effort to uncover the essential features of molecular self-organization that can be

attributed to molecular shape asymmetry, as represented by RM734. We concentrated on a molecular system comprising hard taper-shaped molecules constructed from tangent spheres, where the molecular symmetry is controlled by a parameter called d , representing the ratio between the smallest and largest diameters of the spheres. An analogous hard-sphere model was previously investigated by Greco and Ferrarini [16], as well as by some of us [18]. It involved modeling bend-core-like mesogens using hard crescentlike molecules composed of identical beads. Through purely entropic interactions, this model stabilized another remarkable nematogenic phase known as the twist-bend nematic phase. Our goal was to explore the type of long-range orientational order stabilized by molecular systems exhibiting similar molecular asymmetry to RM734. Similar to the work of Greco and Ferrarini [16] and our own work [18], we focused on examining the role that packing entropy can play in stabilizing such order.

Using Monte Carlo (MC) simulations, we computationally obtained and analyzed self-organization for hard taper-shaped molecules consisting of six tangent spheres. We simulated a wide range of packing densities, spanning from those observed in ordinary liquids to the maximum packing fractions achievable for a given value of d . These maximal packings are represented by continuous lines in Figs. 2 and 3.

More systematically, for packing fractions below $\eta \approx 0.5$, which correspond to the liquid phase, we observed isotropic (Iso), nematic (N), and smectic-A (SmA) phases, as expected for systems built with calamitic molecules. However, we did not observe any polar or splay nematic or smectic phases. This observation was further supported by density functional theory (DFT) calculations and remains valid even in the metastable regime. Moreover, the DFT study suggests that the polar nematic phase is unstable not only for our system but also for other similar systems composed of six tangent balls with a nonzero steric dipole. Our preliminary MC simulations also indicate that even for analogous molecules consisting of up to 11 tangent beads or molecules with a smooth taper surface, there are no significant changes in the predictions. The absence of sterically induced ferroelectric long-range order still persists in these systems.

While a polar smectic-A phase is theoretically possible, it would require unphysically high packing fractions, approximately $\eta \approx 0.8$. An intriguing theoretical prediction involves the potential stabilization of a bilayer smectic phase (SmA₂) at practically the same packing densities characterizing SmA. A similar mesophase was observed in simulations of single-site hard pears [33], but not in our simulations for taper-shaped molecules.

The most striking observation was the presence of complex orientational periodic superstructures, involving hundreds of molecules as depicted in Fig. 9, that couple to the underlying crystalline order of molecular centers at high packing fractions. We label these phases as crystalline polar blue phases. Specifically, for $\eta > 0.5$, the system crystallizes while retaining the layered structure of SmA. Entropically promoted splay, inherently related to the shape of the taper, competes here with the tendency of layers to stay flat. The efficient filling of space depends on the actual value of the parameter d .

For $d \geq 0.75$, when the molecule is not far from the linear tangent hard-sphere (LTHS) hexamer, SmA transforms into a standard nonpolar hexagonal crystal (Cr_{hex}). However, for all $0.75 \leq d < 1$, further compression produces two other crystalline phases with frustrated polar order and periodic splay modulation. For d values around 0.85–0.95 (see Fig. 2), the striped antiferroelectric splay crystal (Cr_SP_A) phase emerges. Within each layer, clusters with macroscopic polarization spontaneously form, but in the adjacent clusters, the polarization is of opposite sign. The clusters are separated by planar defects in the polarization field. For lower values of the d parameter ($0.75 \leq d \leq 0.8$), periodic polar stripes appear, arranged in a checkerboard mesostructure. This structure is referred to as the antiferroelectric double-splay crystal (Cr_{DS}P_A). Again, the alternating polarization pattern facilitates a more efficient molecular packing.

While the splay pattern, coupled with a slight layer deformation, also changes in these two phases, the stabilization of the third phase, called ferroelectric double-splay crystal (Cr_{DS}P_F), relies entirely on significant splay modulation, leading to strongly curved layers. In the Cr_{DS}P_F phase, which is stabilized for $d < 0.75$ directly from SmA, the ferroelectrically polarized splayed clusters form long columns arranged in a checkerboard pattern.

To our knowledge, none of these phases have been previously reported, but theoretical arguments support the existence of related mesophases in a liquid crystalline domain [22,23]. Specifically, Rosseto and Selinger [23] employed the Oseen-Zocher-Frank free energy model, enhanced by the inclusion of flexoelectric coupling between splay and polar order aligned with the director. Additionally, they incorporated a standard Landau free energy expansion based on the polar order parameter. With their theory, they investigated the stability of long-range splay ordering within nematic systems. Their analysis involved evaluating the relative stability of two nematic phases characterized by one-dimensional (1D) and two-dimensional (2D) splay modulations of the director field, respectively. In the 1D case, the system exhibited alternating (infinite) domains of splay and polar order. At interfaces where opposing domains met, both the polar order and splay diminished to zero, resulting in a local director characterized by pure bend deformation. In the 2D case, the double-splay structure was arranged in a 2D checkerboard pattern of alternating polar and splay order. Similarly, along the interfaces, both the polar order and splay went to zero. Both phases were shown to have their range of stability on the phase diagram although the 1D region was fairly small.

Referring to our simulations, none of the predicted orientational splay orderings for nematics have been observed, even though the orientational order of Cr_{DS}P_F resembles that of the nematic double-splay structure. The fundamental difference in orientational ordering becomes apparent at the interfaces. In our case, we observe domain walls, while for the double-splay nematics, the splay and polar orderings decrease to zero, and a pure bend deformation of the director emerges.

The data sets generated and/or analyzed during the current study are available from P.K. upon reasonable request. The source code of an original RAMPACK simulation package used to perform Monte Carlo sampling is available in [68].

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APPENDIX: NONTILTED HEXAGONAL CONFIGURATIONS IN A CLOSE PACKING OF LTHS POLYMERS

We want to establish how one can arrange LTHS polymers in a maximally packed manner, assuming that they form hexatic layers without a tilt (with long molecular axes perpendicular to the layers). A naïve approach would be to prepare hexagonal honeycomb layers and stack them as in the type-B crystal [69], which is observed in systems of spherocylinders [19,54]. However, this configuration is not maximally packed. Therefore, we need to relax two conditions: molecules can deviate slightly from the layers, and hexagons can be slightly deformed. We have identified two such configurations on the basis of the fcc and hcp lattices.

The first configuration is constructed from an fcc lattice of spheres [see Fig. 11(a)]. For polymers consisting of beads k with diameter d , the unit cell has dimensions $d \times d \sqrt{2} \times kd$, and it contains two molecules with geometric

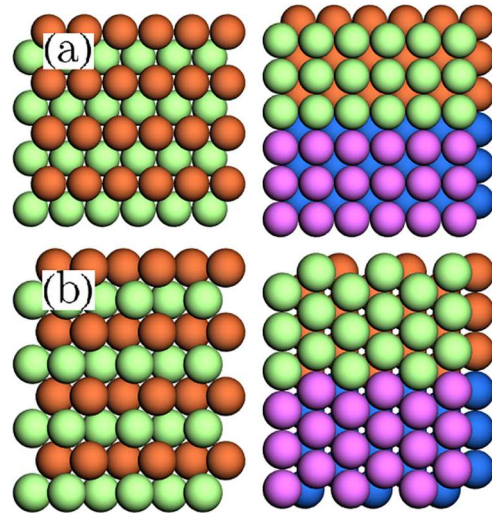


FIG. 11. (a) fcc_B and (b) hcp_B configurations of trimers ($k = 3$). First column is a top view with a visible deformed hexatic arrangement, while the second one is a side view. Colors are to visually separate the molecules.

centers: $(0, 0, kd/2 - d/4)$ and $(d/2, \sqrt{2}/2, kd/2 + d/4)$. We refer to this configuration as fcc_B .

The second configuration is based on the hcp lattice [see Fig. 11(b)]. The unit cell has dimensions $d\sqrt{3} \times 2d\sqrt{6}/3 \times kd$, and it contains four molecules with geometric centers: $(0, 0, kd/2 - d/4)$, $(d\sqrt{3}/3, d\sqrt{6}/3, kd/2 - d/4)$, $(d\sqrt{3}/2, 0, kd/2 + d/4)$, and $(5d/2\sqrt{3}, d\sqrt{6}/3, kd/2 + d/4)$. We refer to this structure as hcp_B .

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Inderdigitation, double twist, and topological defects in a system of hard lollipops

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ABSTRACT

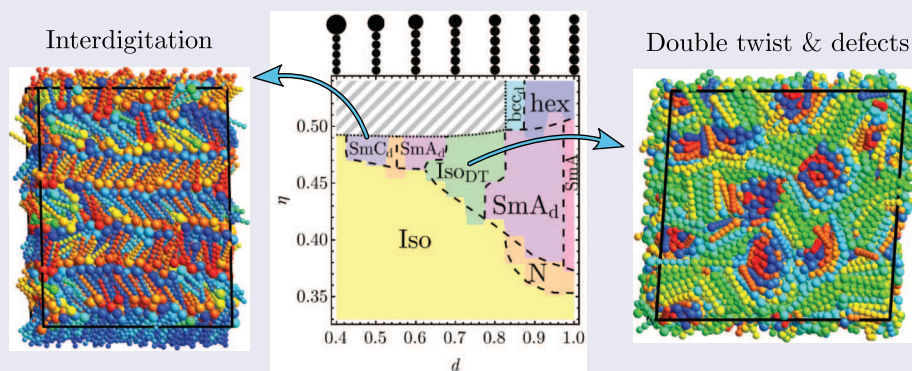
Using hard particle Monte Carlo simulations, we studied a three-dimensional system consisting of identical, lollipop-like particles. Each lollipop was built of five identical, tangent balls placed along a line and one larger ball at one side of the particle and modelled the RM734 molecule, for which ferroelectric and splay nematics were recently discovered in the experiment. Although our model did not recreate these phases, we observed inherently polar type A and C interdigitated smectics. Moreover, an intriguing, isotropic phase consisting of double-twisted clusters joined by planar defects was formed for a moderate packing fraction and ball diameter ratio.

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Lollipops; hard-core interactions; interdigitation; double-twist; topological defects; Monte Carlo



1. Introduction

Although there is no fundamental reason against the formation of a nematic ferroelectric phase in liquids made of elongated molecules with large dipole moments [1,2], it has not been observed until recently [3–6]. Therefore, the discovery started a discussion of the molecular origin of such an alignment of molecules [7,8]. The most straightforward approach requires the violation of the up-down symmetry of a single molecule to provoke such symmetry breaking in the whole phase. In this context, two main options are considered. Symmetry can be violated by either the electrostatic charge distribution along a molecule or its shape. Results of numerical simulations show that ferroelectric structures appear when soft interaction Lennard-Jones or Gay-Berne [9] potentials used to model a taper-like shape of molecules are combined with weak dipole-dipole interactions [10]. For stronger dipoles, however, the bilayer smectic phase is formed [11,12]. This phase

is also observed for systems composed of hard pears [13], which, additionally, exhibit a cubic gyroid phase [14,15].

In the context of the shape effect, it is worth noting that the packing entropy of anisotropic molecules without any additional soft interactions allowed explaining the existence of a variety of liquid crystalline phases starting from the most basic ones like nematics and smectics [16] and ending on twist-bent phases discovered in the second decade of 21st century [17–19]. On the other hand, studies of crystalline phases composed of hard pear- and taper-like molecules show that the splay order, even if observed, cannot propagate uniformly in the whole system [15,20,21]. To optimise the packing fraction, domains of opposite polarities and splay vectors are formed, introducing defects. Point defects in liquid crystalline phases are typically a consequence of some impurities or special preparation of the liquid crystal sample, as they significantly raise

the local free energy. On the other hand, their stability can be assured by the topological charge they carry [22]. Linear defects are observed in blue phases, where the optimal placing on neighbouring molecules requires a non-zero twist between them [23,24]. For some specific value of this twist, molecules form so-called double-twisted tubes where their orientations deviate from the tube axis the more, the farther from it the molecule is. These tubes can form some regular patterns (BPI and BP II) or an isotropic structure (BP III); however, in all these cases, we observe defects at the border of two neighbouring tubes, as the mean local orientation is undefined there. Finally, as mentioned above, planar defects are expected in polar splay phases composed of hard taper-like molecules.

In this study, we want to explore the phase diagram of the system built of lollipop-shaped particles using Monte Carlo simulations. In such a system, one can anticipate the formation of polar phases, which have been observed for similar taper-like molecules but only in the crystalline phase [21]. It is well known that even a slight change in a hard particle's shape can significantly impact the self-assembly structures. One of the best examples is systems composed of hard ellipsoids and similar hard spherocylinders, where a smectic A phase is observed only for the second particle type [25,26]. It is worth noticing that a similar effect also appears in the experimental studies of polar nematics when seemingly insignificant changes are introduced in the molecular structure. For example, although the ferroelectric nematic was observed for RM734 molecules, the phase disappears when the NO₂ group at the end of the molecule is replaced by the CN group [7,27]. In the same spirit, we investigate here a shape that is similar to previously studied taper-like particles [21,28,29] to find out how it affects the existence of particular phases and their range of stability compared to the former systems. The lollipop model is known in the literature, and it was previously studied in two dimensions, where it exhibits standard nematic and various interdigitated smectic A phases, depending on the fine details of the particles' shape [30].

2. Model and methods

2.1. Model particle

To recreate the shape of the RM734 molecule, we use a hard-core toy model created from six co-linear tangent beads (see Figure 1). Among them, five are identical and have a diameter of d , while the last one at the endpoint has a diameter of 1. We restrict d to the range $d \in [0.4, 1]$. Consequently, the shape resembles

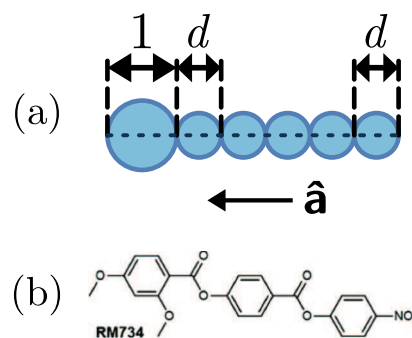


Figure 1. (Colour online) (a) Lollipop particle model: six colinear tangent spherical beads; the first one has diameter 1, while the five remaining ones have a diameter $d \in [0.4, 1.0]$, which is a parameter. Here, $\hat{a}$ is the long molecular axis and the polarisation axis. (b) Taper-shaped RM734 molecule, for which ferroelectric and splay nematics were observed experimentally. Reprinted from Ref. [8] With the permission of the Royal Society of Chemistry.

a lollipop. Its length is $1 + 5d$, while the average ball diameter is $(1 + 5d)/6$, thus, the aspect ratio is constant and equal to 6. Alternatively, if one defines the shape's width as the diameter of the largest ball, the aspect ratio is equal to the length $1 + 5d$.

2.2. Monte Carlo simulations

The system was simulated using Monte Carlo method in the isothermal-isobaric NpT ensemble [16,31,32]. The initial states were prepared as follows. The system was first arranged in an antiferroelectric hexagonal closed-packed (hcp) configuration with layers along the z axis. More precisely, the particles in each honeycomb layer had identical polarisations (the orientations of $\hat{a}$), while at the same time, the polarisations were opposite $\hat{a} \leftrightarrow -\hat{a}$ in the neighbouring layers. Then, the layers were compressed by moving them maximally close to one another without introducing overlaps. As in the hcp configuration, the neighbouring layers are shifted, for $d \leq 0.65$ interdigitated configurations were obtained, where the chains of five smaller balls of "up" and "down" particles were able to fit between themselves. On the contrary, for $d \geq 0.7$, the interdigitation in the hcp configuration was not possible. As for $d \leq 0.65$ we used 12 initial layers, while for $d \geq 0.7$ – six, each configuration had finally six layers (or bi-layers) after the compression. All systems consisted of $N = 4500 - 4800$ particles.

The configurations were then equilibrated for 5×10^8 full MC cycles under a relatively high pressure $p^* = 20$ corresponding to packing fraction $\eta = 0.5 - 0.55$. Here, $p^* = pV_p/(k_B T)$ is the reduced pressure rescaled by the temperature, which is a scale-independent parameter

suitable for hard-core interactions where p/T is the only independent thermodynamic variable. V_p is the particle's volume and k_B is the Boltzmann constant. The equilibrated configurations were then expanded to all target pressures $p^* \in [4, 16]$, covering the phase sequence down to the isotropic liquid. Initial high-pressure $p^* = 20$ configurations were discarded due to the high probability of being metastable jammed states. Additionally, for $d \geq 0.85$, the equilibrated systems with $\eta = 0.45$ were compressed back up to the crystalline phase. Equilibration was extremely slow, requiring up to 10^9 full MC cycles for the densest configurations under investigation. Due to this, we could not obtain the equilibrium crystalline phases in the range $d \in [0.4, 0.8]$ within the reasonable computational timeframe.

Each full MC cycle consisted of one volume move and $1.1N$ particle moves; particle move type was chosen randomly: rototranslation move with the probability $10/11$ and flip move with the probability $1/11$. In the volume move, the box height (along the z axis) and the box base were scaled by two independent, logarithmically sampled factors. For the densest system, the most general triclinic box was used, and volume moves were performed by perturbing all box vectors by small, random displacements. Overlapping configurations were immediately rejected, while the remaining ones were accepted according to the Metropolis-Wood criterion [31,33]

$$P = \min \left\{ 1, \exp \left(N \log \frac{V_1}{V_0} - \frac{p \Delta V}{k_B T} \right) \right\}, \quad (1)$$

where V_0 is the initial system volume, V_1 is the volume after the move and $\Delta V = V_1 - V_0$. A rototranslation move entailed displacing the particle by a random vector and rotating it around a random axis by a random, uniformly sampled clockwise or anticlockwise angle. Finally, during the flip move, the particle was rotated by 180° degrees around the middle of its length so that the molecular axis changed sign $\hat{\mathbf{a}} \leftrightarrow -\hat{\mathbf{a}}$. All particle moves introducing overlaps were rejected, while the rest was accepted. The extents of volume and rototranslation moves were dynamically adjusted so that the acceptance ratio was around 15%, which is the optimal value for hard-core systems [34].

2.3. Order parameters and correlation functions

We introduced a set of order parameters to facilitate the recognition of phases in the system. Nematic order can be measured by the nematic order parameter P_2 . It is obtained by first computing the snapshot-averaged $\mathbf{Q}$ -tensor [35,36]

$$\mathbf{Q} = \frac{1}{N} \sum_{i=1}^N \frac{3}{2} \left(\hat{\mathbf{a}}_i \otimes \hat{\mathbf{a}}_i - \frac{1}{3} \mathbf{I} \right), \quad (2)$$

where $\cdots \otimes \cdots$ is the outer product and $\mathbf{I}$ is the identity matrix. Its eigenvalue with the highest magnitude is an instantaneous P_2 value, and the corresponding eigenvector is the system director. The P_2 parameter is then time-averaged (ensemble-averaged) over independent system snapshots. In the ideal nematic $\langle P_2 \rangle = 1$, for isotropic liquid $\langle P_2 \rangle = 0$, while the minimal value $\langle P_2 \rangle = -0.5$ is reached if all particles are oriented randomly, but orthogonal to the director.

The presence of density undulation can be probed using the smectic order parameter [22]

$$\langle \tau \rangle = \frac{1}{N} \left\langle \max_{h,k,l} \left| \sum_{i=1}^N \exp(\iota \mathbf{k}_{hkl} \cdot \mathbf{r}_i) \right| \right\rangle. \quad (3)$$

Here, ι is the imaginary unit, $\mathbf{r}_i$ is the middle of the i th particle's length, while $\mathbf{k}_{hkl}$ is smectic wavevector. The modulus $|\cdots|$ is computed before averaging in order to eliminate the translational Goldstone mode. Averaging over the independent system snapshots is denoted as $\langle \cdots \rangle$. Allowed, compatible with periodic boundary conditions (PBC) values of $\mathbf{k}_{hkl}$ can be enumerated using the Miller indices h, k, l [37]:

$$\mathbf{k}_{hkl} = h\mathbf{g}_1 + k\mathbf{g}_2 + l\mathbf{g}_3, \quad (4)$$

$$\mathbf{g}_i = \frac{2\pi}{V} (\mathbf{b}_{i+1} \times \mathbf{b}_{i+2}), \quad (5)$$

where $\mathbf{b}_1 \equiv \mathbf{b}_4$, $\mathbf{b}_2 \equiv \mathbf{b}_5$, and $\mathbf{b}_3$ are real-space box vectors and $\mathbf{g}_i$ are reciprocal box vectors. As the initial configurations had six layers, we scanned h, k, l in the range $[-6, 6]$. The smectic order parameter $\langle \tau \rangle$ ranges from 0 for a uniform density to 1 for ideal layers with co-planar $\mathbf{r}_i$.

The formation of antiferroelectric, bilayer, interdigitated arrangement can be registered quantitatively by incorporating the polarisation into a smectic-like order parameter

$$\langle \tau_p \rangle = \frac{1}{N} \left\langle \left| \sum_{i=1}^N (\hat{\mathbf{a}}_i \cdot \hat{\mathbf{n}}) \exp(\iota \mathbf{k}_{hkl} \cdot \mathbf{r}_i) \right| \right\rangle. \quad (6)$$

Here, the exponential function is multiplied by a projection of a long molecular axis onto the global director $\hat{\mathbf{n}}$. By using the same wavevector $\mathbf{k}_{hkl}$ as in τ we probe if each smectic layer separates into two interdigitated sub-layers with different polarisations. It is important to note that choosing the length's middle instead of the mass centre for the computation of both smectic and polarisation order parameters eliminates the artificial separation of "up" and "down" particles due to the mass centre being closer to one end of the shape. The

polarisation order parameter $\langle \tau_p \rangle$ is equal to 0 in an apolar phase and reaches 1 for ideal, equidistant layers with an alternating polarisation.

More information on the structure of the polarisation field can be given by the S_{110} orientational correlation function [38]

$$S_{110}(Z) = \langle \hat{\mathbf{a}}_i \cdot \hat{\mathbf{a}}_j \rangle_{|(\mathbf{r}_j - \mathbf{r}_i) \cdot \hat{\mathbf{z}}| \approx Z}. \quad (7)$$

The averaging is done over all pairs of particles whose distance along the z axis (perpendicular to the layering) is around Z . The minimal value $S_{110} = -1$ is achieved for antiparallel alignment, while the maximal one $S_{110} = 1$ – for parallel.

The tendency to form at least local tetratic or hexatic structures can be measured using the local bond order parameter [39]. In two dimensions, it is defined as

$$\langle \psi_\alpha \rangle = \frac{1}{N} \left\langle \sum_{i=1}^N \frac{1}{\alpha} \left| \sum_{j \in \alpha \text{NN}(i)} \exp(\alpha i \theta_{ij}) \right| \right\rangle, \quad (8)$$

where α is rank, $\alpha \text{NN}(i)$ is a list of α nearest neighbours of i th particle, and θ_{ij} is the angle between the vector joining i th and j th particle, and a constant, arbitrary direction on the plane. For $\alpha = 4$ the tetratic order is measured, while for $\alpha = 6$ – the hexatic. One can generalise the bond order parameter to three-dimensional layered systems by projecting all particles onto their nearest layer and progressing with the original two-dimensional definition. It is important to note that, due to computing the modulus before averaging, local bond order parameters are not equal 0 in disordered systems, but rather $\langle \psi_4 \rangle \approx 0.45$ and $\langle \psi_6 \rangle \approx 0.37$. Ideal tetratic and hexatic configurations render maximal $\langle \psi_\alpha \rangle = 1$ values for their respective ranks α .

Usually, the bond order parameter is defined in a global fashion, where the averaging over the particles and the modulus are swapped:

$$\langle \Psi_\alpha \rangle = \frac{1}{N} \left\langle \left| \sum_{i=1}^N \frac{1}{\alpha} \sum_{j \in \alpha \text{NN}(i)} \exp(\alpha i \theta_{ij}) \right| \right\rangle. \quad (9)$$

Then, the global alignment of bonds is also probed. However, such global order parameter Ψ_α is prone to artificial lowering due to the formation of domains; thus, we revert to using the local version ψ_α .

As the results will show, we observe a globally isotropic phase but with local double-twisted clusters. To detect them, we devise a complex χ order parameter, which is sensitive to the non-zero curl of the director field, consequently called the *curl order parameter*. For i th particle, we define it as

$$\chi_i^{(R)} = \left\langle -i \exp(i \beta_{ij}) \right\rangle_{j: \|\mathbf{r}_{ij}\| \leq R}, \quad (10)$$

where β_{ij} is the directed angle between the vector $\mathbf{r}_{ij} = \mathbf{r}_j - \mathbf{r}_i$ joining centres of i th and j th particle, and the sign-aligned axis $(\hat{\mathbf{a}}_i \cdot \hat{\mathbf{a}}_j / |\hat{\mathbf{a}}_i \cdot \hat{\mathbf{a}}_j|) \hat{\mathbf{a}}_j$ of the j th particle, both projected onto the plane perpendicular to $\hat{\mathbf{a}}_i$. The averaging is performed over all neighbours distant from the i th particle not further than R . The maximal distance R controls the coarse-graining – we choose it to be comparable with the length of the particle; it is dropped in the latter part of the manuscript $\chi_i^{(R)} \equiv \chi_i$. The maximal magnitude $|\chi_i| = 1$ is reached when the angle β_{ij} remains constant, i.e. for a rotationally symmetric director field around the central particle. When $\beta_{ij} = \pm \pi/2$, χ_i is equal ± 1 and the projected field lines are concentric circles. Local deformations of a double-twisted type can be probed by analysing the ensemble-averaged histogram of ψ on a complex plane. A single sharp maximum should be observed around $\chi = 0$ for a uniform system. On the other hand, in the presence of double-twisted clusters, two maxima in $\chi = \pm z$, $z = |z|e^{i\phi}$ will appear.

3. Results

Using the observables and correlation functions described in Section 2.3, as well as the visual inspection of final system snapshots, several phases were recognised in the system. These include: isotropic liquid (Iso), uniform nematic (N), type A smectic (SmA), interdigitated type A smectic (SmA_d), interdigitated type C smectic (SmC_d), isotropic double-twisted cluster fluid (Iso_{DT}), interdigitated bcc crystal (bcc_d) as well as hexatic crystal (hex). Types of phase transitions (e.g. first order, second order) were not recognised due to long simulation times. The phase diagram is shown in Figure 2, while selected order parameters as a function of system parameters are presented in Figure 3. Finally, Figures 4 and 5 show final system snapshots of all recognised phases; among them, Figure 4 depicts the standard phase sequence observed for elongated particles, while Figure 5 gathers less common ones.

3.1. The standard phase sequence

Typically, for elongated particles, one observes the Iso-N-SmA-crystal phase sequence on compression route. Here, it is also the case for $d = 1$ (see Figure 2) constituting for linear tangent hard sphere (LTHS) hexamer [21,40,41], where the radii are identical. The following paragraphs briefly summarise the extent and characteristics of these standard phases.

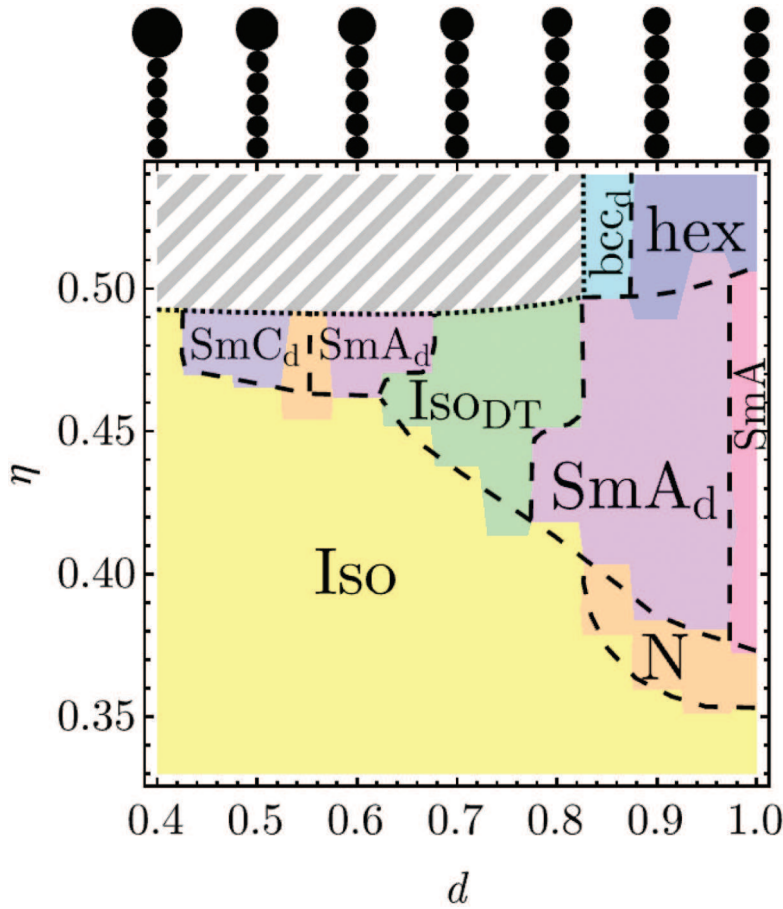


Figure 2. (Colour Online) Phase diagram in the phase space of smaller balls' diameter d and packing fraction η . The following phases are present: isotropic (Iso), uniform nematic (N), type A smectic (SmA), interdigitated type A smectic (SmA_d), interdigitated type C smectic (SmC_d), isotropic double-twisted cluster liquid (IsoDT), interdigitated bcc crystal (bcc_d) and non-polar hexatic crystal (hex). The hatched filling marks the region that was not reached in the simulations due to computational limits.

The isotropic liquid (Figure 4(a)) is observed in a wide range of system parameters. Its border falls monotonically with growing d . For $d = 0.4$, no other phase was observed for packing fractions less than $\eta = 0.5$. For $d = 1.0$, Iso phase is stable until $\eta = 0.35$, where the Iso-N phase transition occurs. All order parameters are close to their disorder value (see Figure (3)). One can observe a slight increase of nematic $\langle P_2 \rangle$ and smectic $\langle \tau \rangle$ order parameters (Figure 3(a,b)) near the phase boundary.

The nematic phase (Figure 4(b)), adjacent to Iso, occurs only in a narrow range of d and η . For $d \leq 0.85$ it is completely absent (except for $d = 0.55$, which is discussed later). It is signified by a large value of the nematic order parameter $\langle P_2 \rangle \approx 0.6 - 0.7$, being near the upper limit of a typical range $\langle P_2 \rangle \in [0.3, 0.7]$ observed in the experiments. Comparable values of $\langle P_2 \rangle$ were measured in analogous studies of tapers [21,29]. The smectic order is near zero. A quick destabilisation of the N phase with decreasing d is surprising, as for $d = 0.8$ the particle is visually almost indistinguishable

from the $d = 1$ case (cf. Figure (2)). On one hand, LTHS hexamer is the first of the LTHS k -mer family which stabilises the nematic phase (for $k \leq 5$ SmA is formed directly over Iso), thus the N phase may be susceptible to slight variations of particle's shape. On the other hand, in the study of tapers [21], the N phase appears even for shapes with a high anisotropy of balls' radii.

A standard type A smectic appears over the N phase only for $d = 1$ (Figure 4(c)); for lower d values, all smectics exhibit a varying but non-zero degree of interdigitation, which is discussed later. Nematic order is nearly perfect with $\langle P_2 \rangle$ close to 1. Smectic order is significant, which is confirmed by $\langle \tau \rangle$ increasing from $\langle \tau \rangle \approx 0.55$ to nearly 1 upon compression. One also observes a rise of local hexatic order signified by $\langle \psi_6 \rangle$ reaching ≈ 0.58 near the upper phase boundary; the preference of having six neighbours facilitates more optimal local packing; however, inspection of system snapshots does not reveal long-range hexatic order, as, e.g. in the SmB phase [42]. Polarisation order $\langle \tau_p \rangle$ is, by definition, zero since the particle is non-polar.

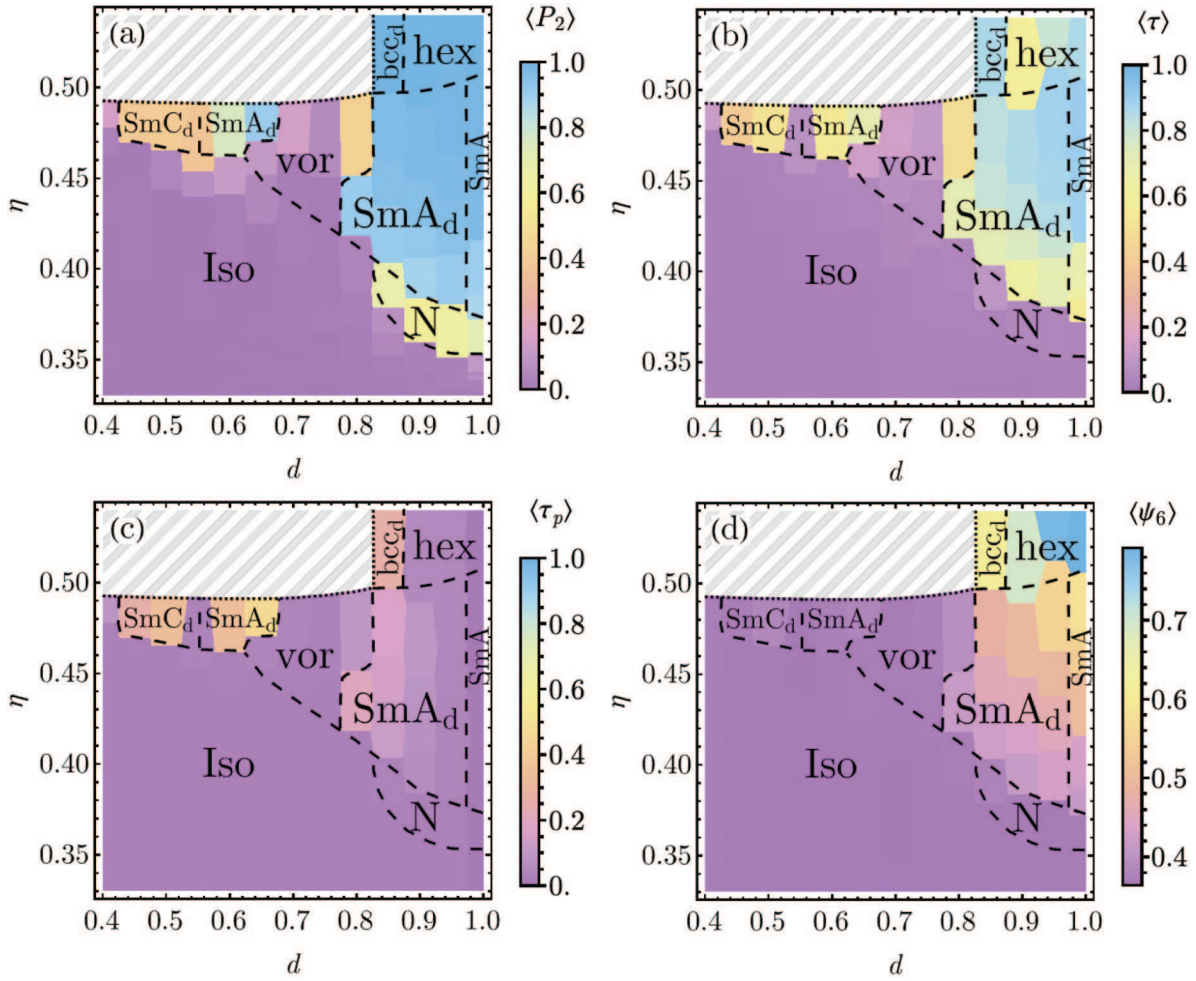


Figure 3. (Colour online) The dependence of selected observables on the smaller balls' diameter d and packing fraction η : (a) nematic order parameter $\langle P_2 \rangle$, (b) smectic order parameter $\langle \tau \rangle$, (c) polarisation order parameter $\langle \tau_p \rangle$ and (d) local hexatic bond order parameter $\langle \psi_6 \rangle$. The hatched filling marks the region that was not reached in the simulations due to computational limits.

A non-polar hexatic crystalline phase is observed over $\eta = 0.5$ for $d \geq 0.9$ (Figure 4(d)). High local hexatic order is confirmed by values of $\langle \psi_6 \rangle > 0.7$ and reaching close to 1 for $d = 1$. Moreover, as it can be inferred from system snapshots, the hexatic order is actually long-range. The hex phase is formed by stacking hexagonal honeycomb layers on top of one another, with at most local correlations of particles' polarisation. The values of $\langle P_2 \rangle$ and $\langle \tau \rangle$ are high, although $\langle \tau \rangle$ falls to ≈ 0.6 for $d = 0.9$. In this case, the system slightly resembles the hexatic columnar Col_h phase [43]. However, the columnar phase remains a liquid in the direction of columns, and $\langle \tau \rangle$ consequently falls to 0, while here the system is jammed, and a non-zero equilibrium value of $\langle \tau \rangle$ is reached.

3.2. Interdigitated phases

For $d < 1$, the particle ceases to possess the up-down symmetry. Consequently, polar phases may emerge.

Phases with a bulk, non-zero polarisation were recently discovered for the RM734 molecule [5], among which the most important one is the ferroelectric nematic N_F . It is widely believed that the most important molecular factors responsible for stabilising the N_F phase are the taper-like shape of the mesogen as well as a large dipolar moment of the molecule [7]. Another polar phase appearing in the phase sequence of RM734 is splay nematic N_S , where the bulk polarisation is zero; however, one observes alternating areas with non-zero polarisation and a presence of splay modulation. De Gregorio et al. [28] argued, basing on the second-order density functional theory (DTF), that a taper-like shape of the particle is enough to promote long-range splay in the system. The shape effect has been studied numerically by our research group in two recent papers [21,29] treating similar particles as in the current study built of six or 11 hard tangent balls; however, with linearly increasing radii (notably, the 11-ball model was

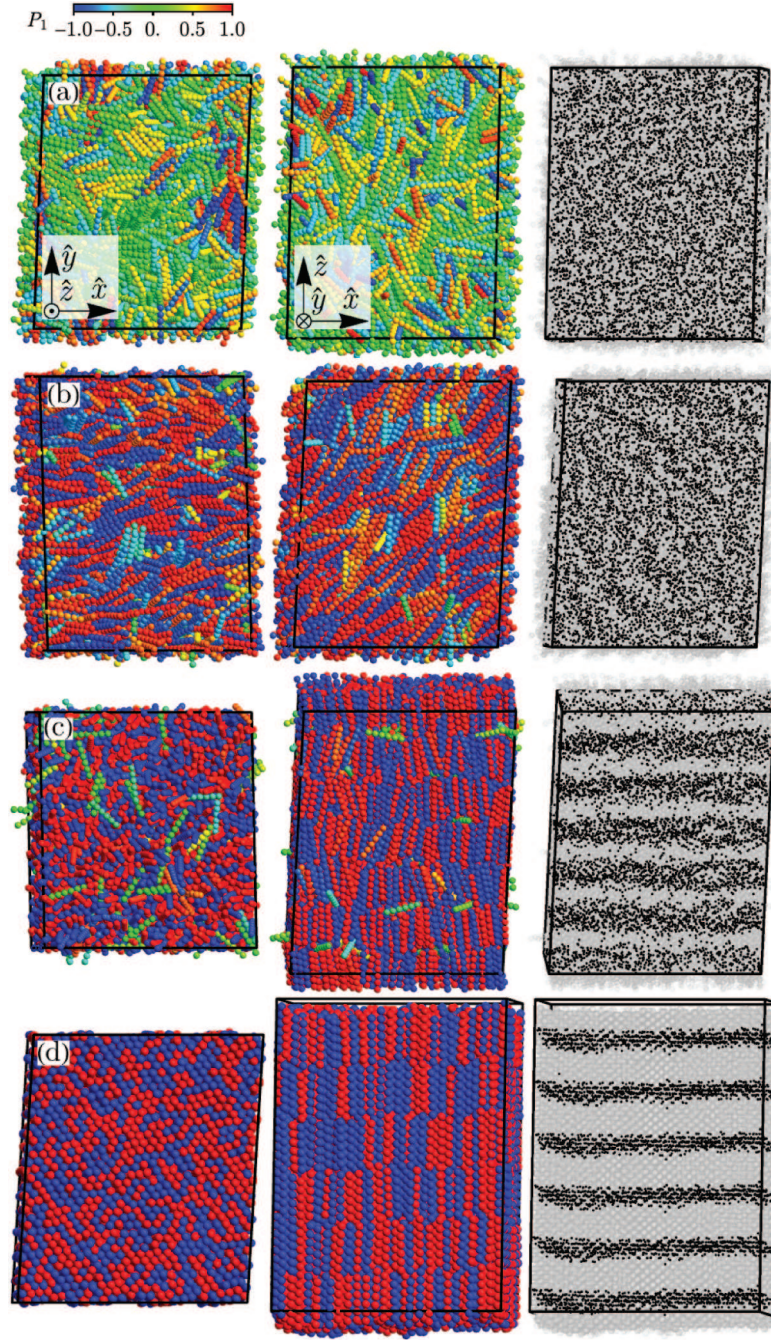


Figure 4. (Colour online) System snapshots of the phase sequence in a system of linear tangent hard sphere (LTHS) hexamers ($d = 1$), common for elongated particles. Left and middle columns are, respectively, top and side views of the simulation box; the bottom edge of the box in the top view is the top edge in the side view. The right column shows the side view with geometric centres (black dots). The particles are colour-coded according to $P_1 = \hat{n} \cdot \hat{a}$. Subsequent rows show the compression sequence: (a) Iso ($\eta = 0.34$), (b) N ($\eta = 0.36$), (c) SmA ($\eta = 0.39$) and (d) hex ($\eta = 0.54$).

identical as in the DFT study [28]). It was shown that for such particles, entropic interactions are not enough to stabilise either N_F or N_S phases.

Similarly, in our system of lollipops, neither nematic nor smectic ferroelectric or splay phases are observed. However, antiferroelectric, interdigitated smectics SmA_d and SmC_d , as well as bcc_d crystal appear. A polar

interdigitated smectic is formed by superimposing two phase-shifted smectics with the same mean density and period but with different polarisations [44]. In first order, the density profile $\rho(z, s)$ can be described as

$$\rho(z, +1) = \frac{\rho}{2} + \frac{\rho}{2} \tilde{r} \sin(kz), \quad (11)$$

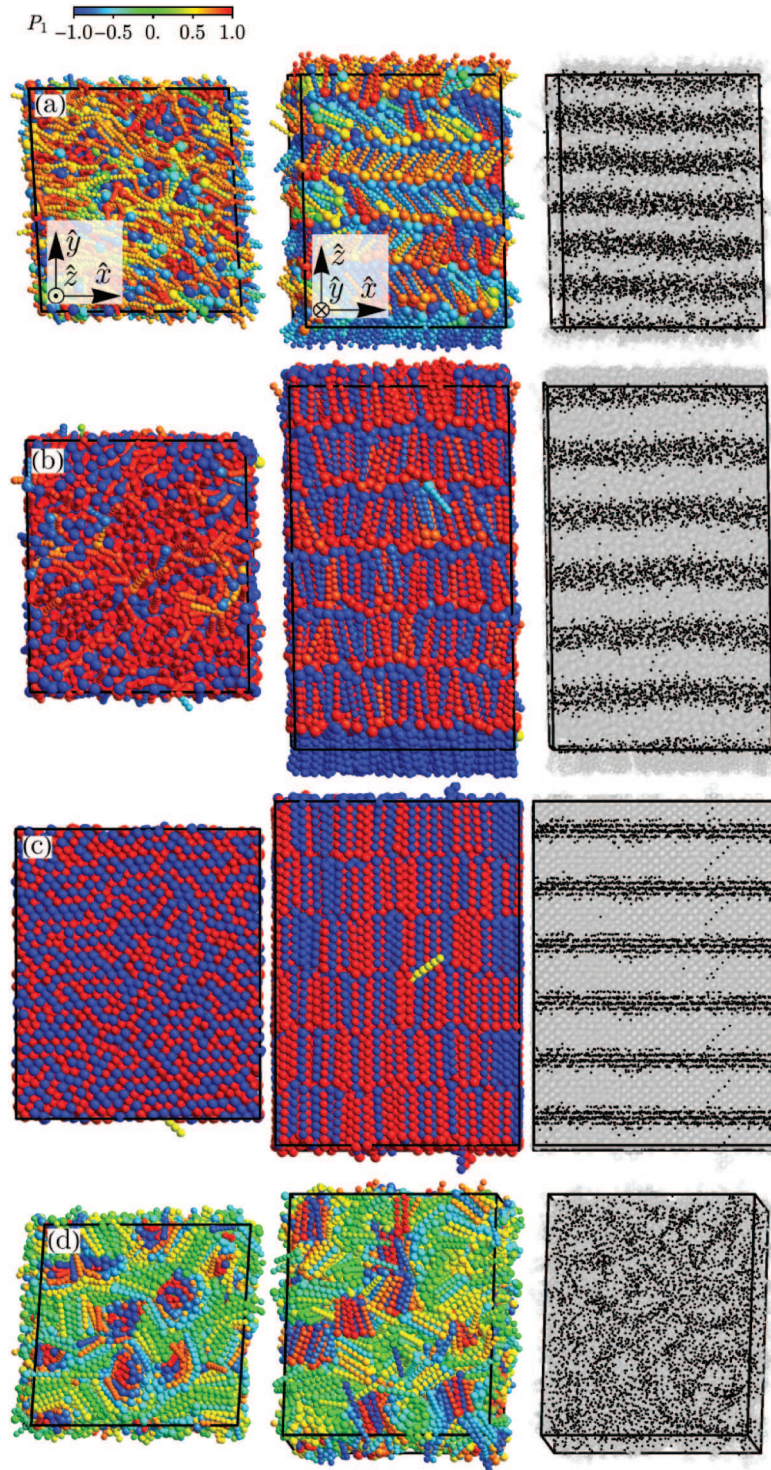


Figure 5. (Colour online) Snapshots of phases different than the ones observed for $d = 1$ (Figure 4). The panel follows the same layout as Figure 4 (columns, from the left: top view, side view, side view of geometric centres). Subsequent rows correspond to: (a) SmA_d $[(d, \eta) = (0.65, 0.48)]$, (b) SmC_d $[(d, \eta) = (0.5, 0.48)]$, (c) bcc_d $[(d, \eta) = (0.85, 0.52)]$ and (d) Iso_{DT} $[(d, \eta) = (0.75, 0.46)]$.

$$\rho(z, -1) = \frac{\rho}{2} + \frac{\rho}{2} \tilde{\tau} \sin[k(z - \Delta z)], \quad (12)$$

where the ideal nematic order is assumed, $s = \hat{\mathbf{a}}_i \cdot \hat{\mathbf{n}} = \pm 1$, $\rho = \eta/V_p$ is the mean number density, $\tilde{\tau} \in [0, 1]$ controls the depth of undulations, and Δz is the distance between the maximal densities for opposite polarisation. The total density profile is then equal

$$\rho(z) = \sum_{s=\pm 1} \rho(z, s) = \rho + \rho \tau \sin\left[k\left(z - \frac{\Delta z}{2}\right)\right], \quad (13)$$

where $\tau = \tilde{\tau} \cos(k\Delta z/2)$. The structure has a non-zero value of the polarisation order parameter

$$\tau_p = \frac{1}{\rho p} \left| \sum_{s=\pm 1} \int_0^p dz s \exp(i k z) \rho(z, s) \right| = \frac{\tilde{\tau}}{2} \left| \sin\left(\frac{k\Delta z}{2}\right) \right|, \quad (14)$$

where $p = 2\pi/k$ is the layer width (the period). Clearly, the value of τ_p grows with Δz and is zero for $\Delta z = 0$, when the interdigitation disappears.

One of the interdigitated phases, the type C interdigitated smectic SmC_d appears in the range $d \in [0.45, 0.5]$ for packing fractions $\eta > 0.47$. Its snapshot is presented in Figure 5(a). The director $\hat{\mathbf{n}}$ within each layer is tilted from the smectic wavevector $\mathbf{k}$, $\hat{\mathbf{n}} \nparallel \mathbf{k}$. The tilt angle is nearly constant, but the direction alternates in the neighbouring layer, which means that the smectic is anticlinic (SmC_A) [45,46]. It is reflected in a significantly smaller value of the nematic order parameter $\langle P_2 \rangle \approx 0.4$ (Figure 3(a)) than in other smectic and crystalline phases. Each layer separates into two components with opposite polarisations. The interdigitation can be clearly seen in the snapshot as well as in Figure 6(a), where the numerical, ensemble-averaged density profiles $\rho(z, s)$ are presented separately for $s = +1$ and -1 . The separation Δz is large, near one-third of the period p . The density peaks are not identical for all layers. Most probably, it can be attributed to sporadic structure defects visible in some of the layers (cf. Figure 5(a)) and fluctuations of the tilt angle. Interdigitation is further signified by a non-zero value of the polarisation order parameter $\langle \tau_p \rangle \approx 0.35$ (Figure 5(c)). Last but not least, we observe a non-trivial profile of the S_{110} correlation function (red solid line in Figure 7(a)). The maxima for the distances $Z = 2Kp$, $K \in \mathbb{Z}$ are equal ≈ 0.3 and are higher than for $Z = (2K + 1)p$, which are equal ≈ 0.15 ; the first set corresponds to correlations between the layers with an identical tilt, while the second one – to opposite tilts, which explains the lower value. In between the maxima, there are minima with $S_{110} \approx -0.35$ for

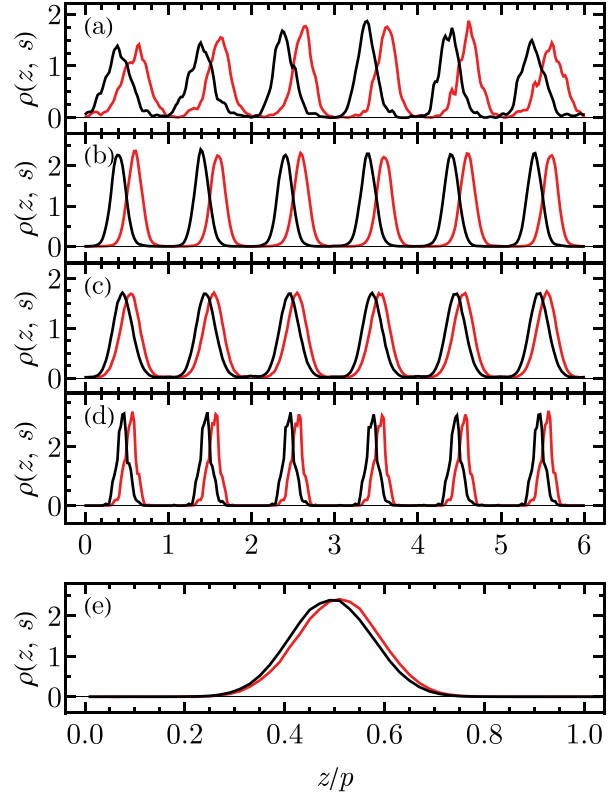


Figure 6. (Colour online) Normalised particle density $\rho(z, +1)$ of “up” particles (red line) and $\rho(z, -1)$ of “down” particles (black line) as a function of z coordinate rescaled by the layers’ width p (the period) for (a) SmC_d $[(d, \eta) = (0.55, 0.48)]$, (b) SmA_d $[(d, \eta) = (0.65, 0.48)]$, (c) SmA_d $[(d, \eta) = (0.8, 0.44)]$, (d) bcc_d $[(d, \eta) = (0.85, 0.52)]$ and (e) SmA_d $[(d, \eta) = (0.95, 0.45)]$. In the last (e) panel, only a single period is shown.

$Z \approx (2K + 0.4)p, (2K + 1.6)p$, which further proves the existence of sub-layers with a different polarisation.

Type A interdigitated smectic SmA_d (see Figure 5(b) for a system snapshot) is observed in two regions of the phase diagram, separated by another phase (isotropic double-twisted cluster liquid, discussed in the next subsection). The smaller region appears for $d \in [0.6, 0.65]$ and $\eta > 0.46$, while the second, larger one for $d \in [0.8, 0.95]$ and $\eta > 0.38$. Here, the director $\hat{\mathbf{n}}$ is parallel to the smectic wavevector $\mathbf{k}$, $\hat{\mathbf{n}} \parallel \mathbf{k}$ and both nematic order $\langle P_2 \rangle$ and smectic order $\langle \tau \rangle$ parameters have relatively large values ($\langle P_2 \rangle > 0.75$ and $\langle \tau \rangle > 0.55$). Alike the SmC_d phase, the interdigitation is reflected in the observables and the correlation functions. Figure 6(b,c,e) presents the density distribution $\rho(z, s)$ for one point in the SmA_d region for lower d values and two points in the second SmA_d region for higher d values. In all three cases, the density peaks are smooth and nearly identical for all six layers. The separation Δz falls with increasing d , with $\Delta z \approx 0.2p$ for $d = 0.65p$, $\Delta z \approx 0.15$ for $d = 0.8$ and $\Delta z \approx 0.03p$ for $d = 0.95$. It is worth noting that even for the highest

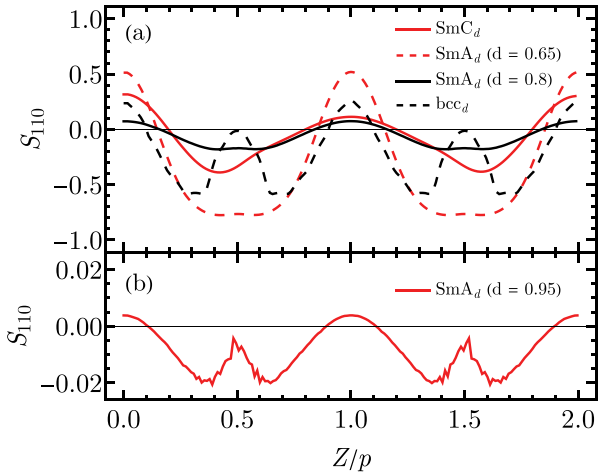


Figure 7. (Colour online) The dependence of S_{110} correlation function on the distance Z along the z axis rescaled by the period p (layers' width) for different system parameters. Only the first two $Z \in [0, 2p]$ of the six periods fitting in the box are shown; two further period pairs $Z \in [2p, 4p]$ and $Z \in [4p, 6p]$ are nearly identical. (a) The dependence for: red solid line – SmC_d $[(d, \eta) = (0.55, 0.48)]$, red dashed line – SmA_d $[(d, \eta) = (0.65, 0.48)]$, black solid line – SmA_d $[(d, \eta) = (0.8, 0.44)]$, black dashed line – bcc_d $[(d, \eta) = (0.85, 0.52)]$. (b) The dependence for SmA_d $[(d, \eta) = (0.95, 0.45)]$ on a magnified scale. Here, an additional averaging is performed over three period pairs $Z \in [Kp, (K+2)p]$, $K = 0, 2, 4$, for improved statistics.

$d < 1$ studied, $d = 0.95$, the interdigitation minuscule as it may be, it is clearly visible over the statistical fluctuations (which are smaller than the line width in Figure 6(e)). It leads us to believe that the SmA_d phase may be present for each $d < 1$, regardless of how close to 1 the d is. The polarisation order parameter (Figure 3(c)) is visibly larger than 0 for all $d < 0.95$ and mostly rises with falling d (excluding the $d = 0.6$ case), reaching $\langle \tau_p \rangle \approx 0.5$ for $d = 0.65$. For $d = 0.95$, its value is indistinguishable from the non-polar case within statistical error bounds. The analysis of S_{110} correlation function for the same points (red dashed and black solid lines in Figure 7(a), as well as the only line in Figure 7(b)) also confirms the interdigitation pattern. All three cases presented are qualitatively similar – the maxima appear for $\Delta Z = Kp$, $K \in \mathbb{Z}$ and deeper, wider valleys originating from the opposite polarisations are placed around $\Delta Z = (K + 0.5)p$. Exactly in $\Delta Z = (K + 0.5)p$, one can observe additional, small maxima. As it can be seen, e.g. in the snapshot from Figure 5(b), there are hardly any particles between the layers, and if they appear, they are usually tilted w.r.t. the director. In such a case, S_{110} is higher than for the antiparallel alignment, explaining the presence of these small maxima. They are visible most clearly for $d = 0.95$ (Figure 7(b)), where the overall values of S_{110} are close to 0; one can also see significantly larger fluctuation in these regions in

comparison to $\Delta Z \approx Kp$. Lastly, similarly to the standard SmA smectic for $d = 1$, for $d > 0.8$, a rise of the local hexatic order parameter $\langle \psi_6 \rangle$ is observed (Figure 3(d)). However, once again, hexatic correlations are at most local.

Between the SmA_d and SmC_d phases, for $d = 0.55$, the system fails to create a smectic phase, and instead a high-density nematic is formed (as signified by a high $\langle P_2 \rangle$ and a low $\langle \tau \rangle$ values, c.f. Figure 3(a,b)). The layering present in the initial configuration is destroyed during the course of a simulation. Inspection of the simulation trajectory (results not shown) reveals that small, local smectic clusters are formed. This hints that the culprit may be the competition between type A and C smectics, in which the angles between the director $\hat{n}$ and the wavevector $\mathbf{k}$ are different. However, one can never exclude the possibility that the system may have become jammed in a metastable configuration, requiring significantly more simulation cycles to relax and rebuild well-defined layers, which is beyond our computational limits.

Finally, we present the reasoning why one observes the SmC phase for smaller d values and SmA for larger ones, as well as what is the origin of the interdigitation. Both effects may be attributed to the packing efficiency. The mean distance between the particles is imposed by the largest balls. Then, however, the chains of smaller ones are packed suboptimally. The remedy is the superposition of two oppositely polarised structures. That way, there are two times more chains to pack in the layer. Moreover, all large balls are in contact, which helps them to arrange more optimally among themselves. For small d values, this mechanism is not sufficient enough. However, introducing the tilt mitigates the issue – the layers' width and, consequently, their volume is decreased, allowing once again for a better packing of the chains. The same effect was observed in the two-dimensional system of lollipops [30].

The last phase with the interdigitation of oppositely polarised substructures is the tetragonal crystalline phase (Figure 5(c)). It is formed by superimposing two tetragonal lattices with opposite polarisations, shifted in X and Y direction by half of the unit cell size. Thus, we call the structure *interdigitated body-centred cubic crystal* (bcc_d), although one has to remember that the distances between interdigitated counterparts are asymmetric in the z direction. It should be noted that the snapshot contains some defects, including multi-domain structure and columns of particles protruding from layers. The number of defects decreases with the number of cycles performed, however we were not able to eliminate them fully due to restricted time and computational resources. Interdigitation is confirmed by the $\rho(z, s)$ density profile (Figure 6(d)), non-zero value of $\langle \tau_p \rangle$ as well as S_{110} correlation function (black dashed line in Figure 7(a)). In the case of the S_{110}

function, well pronounced maxima for $\Delta Z = (K + 0.5)p$ can be probably again attributed to the outliers with anomalous orientations placed in between the layers. Tetratic order is confirmed by the local tetratic order parameter $\langle \psi_4 \rangle \approx 0.72$ (result not shown), which is significantly larger than for all other simulation points. Hexatic order parameter also has a significant value $\langle \psi_6 \rangle \approx 0.65$. This phenomenon can be explained by noticing that the projection of bcc structure on a plane essentially creates flattened hexagons, which is consequently detected by $\langle \psi_6 \rangle$.

3.3. The isotropic double-twisted cluster liquid

The two SmA_d regions are separated by a phase for which all ensemble-averaged values of order parameters ($\langle P_2 \rangle$, $\langle \tau \rangle$, $\langle \tau_p \rangle$ and $\langle \psi_6 \rangle$) in Figure 3 are close to their disorder values. This suggests that the phase is globally isotropic. However, the inspection of the system snapshot (Figure 5(d)) reveals some mesostructure. The system consists of small clusters with a size comparable to the particle's length. Each cluster has a local, preferred direction $\hat{n}_c$. We will be calling the plane perpendicular to $\hat{n}_c$ the *cluster plane*. The analysis of clusters' structure reveals that the long molecular axes $\hat{a}_i$ are tilted in the direction tangent to a family of circles lying in the cluster plane, centred around the cluster centre $\mathbf{r}_c$. Moreover, the tilt increases with the distance from $\mathbf{r}_c$. The sense of the axes $\hat{a}_i$ is random; thus, the phase appears to be apolar. The structure of the director field in the cluster is illustrated in Figure 8(a). Consequently, the projections $\tilde{\mathbf{a}}_i = \hat{\mathbf{a}}_i - \hat{n}_c(\hat{n}_c \cdot \hat{\mathbf{a}}_i)$ of the axes $\hat{\mathbf{a}}_i$ of the particles surrounding the centre $\mathbf{r}_c$ are tangent to the same family of circles and the length of $\tilde{\mathbf{a}}_i$ vectors increases with the distance from $\mathbf{r}_c$. The projections are illustrated in Figure 8(b).

The director field modulation described above is known in the literature as *double-twist* [47,48]. Double-twist is observed in many systems, among which the

most known are the blue phases (BP). The director field in type I, II and III BP forms long, double twisted tubes with linear topological defects between them (the *disclinations*). While disclinations in type I and II BP form a regular lattice, type III is disordered, which bears the most resemblance to our system. The main difference is the length scale – while the size of our clusters is comparable to the particles' length, the modulations in blue phases are usually on the scale of hundreds of particles.

To reflect the most important features of the phase described in this section, we call it the *isotropic double-twist cluster liquid* (Iso_{DT}). The double-twisted clusters appearing in Iso_{DT} are readily detected by the curl order parameter χ (10). Its histogram on a complex plane is shown in Figure 9. Panel 9a shows χ for the standard isotropic liquid. As expected, χ is close to 0 for most particles. The spread of the peak can be attributed to statistical fluctuation, due to which a local double-twisted structure may be momentarily formed. The situation changes in the Iso_{DT} phase (Figure 9(b)). Here, the system's most probable values of χ are $\approx \pm 0.8$. It means that most particles belong to double-twisted clusters. As the preferred values of χ lie on the real axis, it is confirmed that the tilt direction (the $\tilde{\mathbf{a}}_i$ projected vector) is tangent to the concentric circles. The values of χ with an opposite complex phase correspond to clusters with a different chirality (relative to the central particle's polarisation).

A closer inspection of the Iso_{DT} phase system snapshot (Figure 5(d)) reveals a local density modulation. The density profile is, however, not periodic as for smectics observed in the system in other regions of the phase diagram. To gain more insight into the density modulation, we computed the radial distribution function $G(r)$ [38]. The comparison of $G(r)$ for Iso_{DT}, Iso and SmA phases is presented in Figure 10. For the Iso phase (black dashed line), we observe a few short-ranged maxima and minima separated by $\Delta r \approx 0.2l(d)$, where $l(d)$ is the length of the particle, which roughly corresponds to the

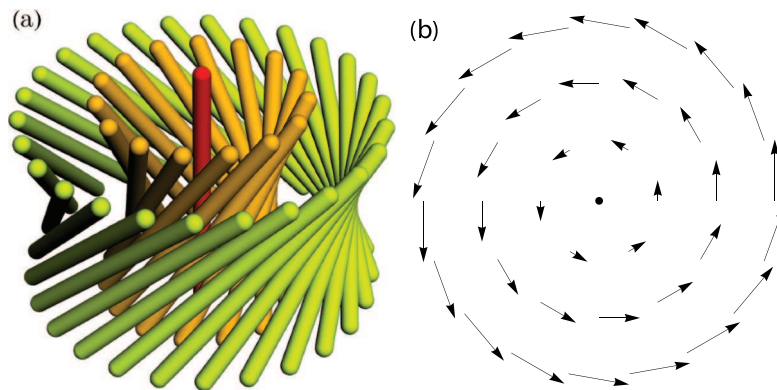


Figure 8. (Colour online) (a) Illustrative representation of the preferred directions in the cluster. The tilt of the director increases with the distance from the middle. (b) Projections of the director on a cluster plane. The field lines of an ideal field form concentric circles around the cluster centre $\mathbf{r}_c$. In such a configuration, the curl order parameter χ [Equation. (10)] reaches its maximal magnitude $|\chi| = 1$.

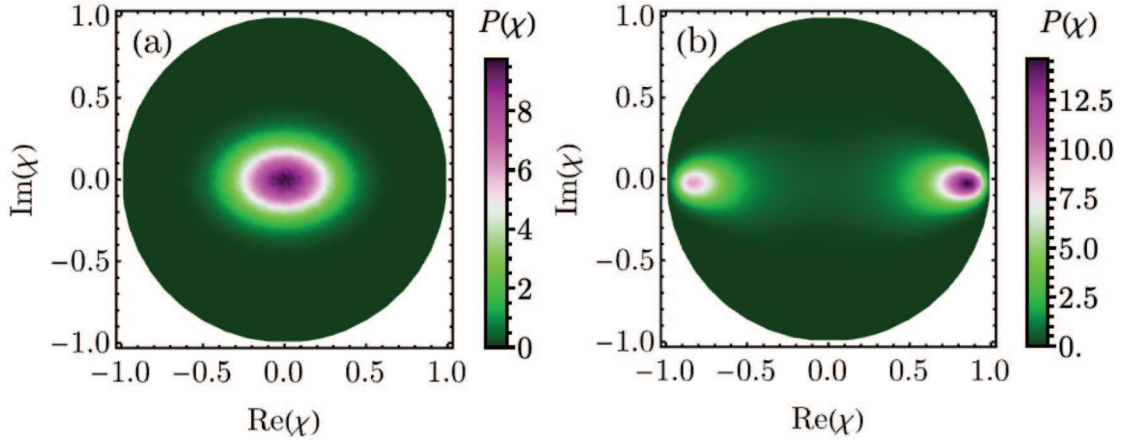


Figure 9. (Colour online) Histograms of the curl order parameter χ on a complex plane for selected parameter sets: (a) Iso $[(d, \eta) = (0.75, 0.35)]$ and (b) Iso_{DT} $[(d, \eta) = (0.75, 0.46)]$.

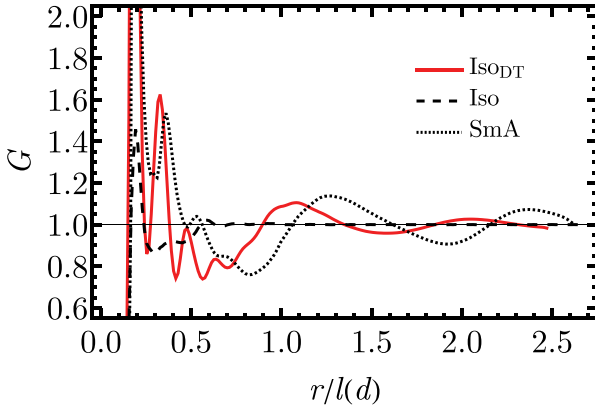


Figure 10. (Colour online) The dependence of the radial distribution function $G(r)$ on the distance r in the units of the particles length $l(d)$ for selected phases: red solid line – Iso_{DT} $[(d, \eta) = (0.75, 0.46)]$, black dashed line – iso $[(d, \eta) = (0.75, 0.35)]$ and black dotted line – SmA $[(d, \eta) = (1, 0.39)]$. Horizontal black line marks the value $G(\infty) = 1$.

width of the particle. The modulations vanish before r reaches $l(d)$ value. On the other hand, the SmA phase (black dotted line) behaves differently. Short-ranged minima and maxima with $\Delta r \approx 0.2l(d)$ separation are significantly more pronounced. Moreover, a second series of maxima appears with separation $\Delta r \approx 1.2l(d)$, which originates from the layering of the system. By comparing the $G(r)$ profile of Iso_{DT} (red solid line) with the two other phases, one clearly sees that it is closer to the SmA case. In particular, we observe secondary maxima with the separation $\Delta r \approx l(d)$. This means that the Iso_{DT} phase may be described as locally smectic-like.

The existence of the Iso_{DT} phase can be explained by the observation that in the nematic and smectic phases, the effective shape of the elongated particles thermally vibrating around the director resembles an hourglass [48]. The

double-twisted configuration is a natural way to pack particles with such a shape. In the system of lollipops, the hourglass shape effect may be amplified by the formation of pairs of lollipops with an opposite polarisation. Moreover, the tilt inherent to the double-twist, as we discussed in Sec. 3.2, increases the packing efficiency of small molecules' chains. The Iso_{DT} phase is in direct competition with the type A interdigitated smectic SmA_d. Both phases rely on different mechanisms to increase the packing entropy. The ones providing a larger gain decide which of the two phases is eventually formed.

4. Summary and outlook

In this manuscript, we have analysed the system of hard particles built of six tangent balls, whose shape resembles a lollipop. The particles modelled the RM734 molecule, for which ferroelectric and splay polar nematics were observed in recent experiments. The systems were simulated using the isothermal-isobaric Monte Carlo sampling in the orthorhombic as well as the general triclinic simulation boxes. We varied two independent parameters: the packing fraction η and the diameter of the smaller balls d , while keeping the diameter of the largest ball constant and equal one. The phases present in the system were identified by inspection of system snapshots, together with the computation of expectation values of order parameters, such as the nematic order parameter $\langle P_2 \rangle$, smectic order parameter $\langle \tau \rangle$, polarisation order parameter $\langle \tau_p \rangle$, and bond order parameters $\langle \psi_4 \rangle$, $\langle \psi_6 \rangle$, as well as S_{110} correlation function, radial distribution function $G(r)$, the density profile $\rho(z, s)$, and histograms of the curl order parameter χ . Apart from a standard phase sequence Iso-N-SmA-

crystal, commonly observed for elongated particles, we identified four other phases. The first group was three interdigitated phases: type A and C interdigitated smectics (SmA_d and SmC_d , respectively) as well as interdigitated body centred cubic crystal (bcc_d). All of them were composed of two sets of oppositely polarised smectic or crystalline layers with a slight spatial dephasing between them, which in consequence made those phases polar. It is worth noting that for a similar system with taper-like particles [21,29], no liquid crystalline polar phases were observed. The fourth, and arguably the most intriguing phase, was the isotropic double-twist cluster liquid (Iso_{DT}). It was built of small clusters of particles twisting around the centre; the clusters were oriented isotropically and spatially uncorrelated, resembling type III blue phase, but on a much smaller scale. The phase was locally smectic-like; however, the density modulations did not create any periodic pattern.

The manuscript contributed to a better understanding of the shape effect of particles with a broken up-down symmetry, which has been of particular interest in recent years. This model has a potential for further expansions, which include identifying the phases in the regions of the phase diagram not reached in this study, as well as exploration of its other variants, such as a different number of spheres or a smooth surface. Moreover, based on the observation that the phase diagrams of lollipops and tapers are vastly different, studying the self-assembly of other particles with a broken up-down symmetry may result in the observation of many novel phases.

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Disclosure statement

No potential conflict of interest was reported by the author(s).

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Code availability statement

The source code of an original RAMPACK simulation package used to perform Monte Carlo sampling is available at <https://github.com/PKua007/rampack>.

Data availability statement

The datasets generated during and/or analysed during the current study are available from P.K. upon reasonable request.

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