Phases with splay modulation in a system of hard wedges composed of balls

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We studied equilibrium systems composed of wedge-shaped monodisperse molecules using hard-particle Monte Carlo simulations. Each model molecule was made up of six colinear tangent spheres with linearly decreasing diameters. Thus, the shape was unequivocally described by a single parameter \( d \): the ratio of the smallest and largest diameters of the spheres. The phases of the systems were analyzed as a function of \( d \) and packing density \( \eta \). As interactions were purely of the excluded volume type, the emergent phases were governed solely by the configurational entropy. For \( \eta < 0.5 \), in addition to the isotropic liquid, we observed standard nematic and smectic A liquid crystalline phases. However, for \( \eta > 0.5 \), apart from the ordinary non-polar hexagonal crystal, three new frustrated polar crystalline phases with splay modulation appeared: antiferroelectric splay crystal (Cr\(_5\)P\(_A\)), antiferroelectric double splay crystal (Cr\(_{DS}P\(_A\)) and ferroelectric double splay crystal (Cr\(_{DS}P\(_F\)). All configurations were studied in terms of nematic, smectic, and hexatic order parameters, as well as the radial distribution function and the polarization correlation function.

I. INTRODUCTION

Random packings of hard objects appear in a broad range of fundamental and applied sciences, mainly in the modeling of granular matter, but also in studies of the self-assembly of nano-particles that are important for the stability of liquid crystal phases and glass formation
[1, 2]. It is known that even small differences in the shapes of particles may have a significant impact on the properties of the assembly they form. For example, a smectic phase is formed in the system made up of spherocylinders [3], but not ellipsoids of a very similar shape [4]. Some liquid-crystalline phases can be explained solely by the entropic effects of the shapes forming them, without reference to any other physical soft interaction. One of the recent examples of this approach is the explanation of twist-bent nematic phase formation in a system composed of bow-shaped molecules [5, 7]. On the other hand, recent experiments prove the existence of long-range polar order in nematic liquid crystals [8], which initiated the debate about the molecular origins that lead to such self-organization [9].

Years earlier, Meyer showed that a geometric asymmetry of the molecules should lead to a flexoelectric effect which, in liquid crystals, couples splay and bend director deformations to an electric polarization [10]. Therefore, a candidate molecule that leads to the formation of polar structures should be characterized by some distribution of electric or steric dipoles. Natural candidates belonging to the first category are pear-shaped or wedge-shaped particles. Numerical simulations of systems built of such molecules began in the last decade of the twentieth century [11, 12]. There, polarity at the molecular level was induced by an interaction potential between molecules combining two rigidly connected centers, an ellipsoidal Gay-Berne [13] and a spherical Lennard-Jones. For such a system, anti-parallel alignment was observed. Fine-tuning of potential parameters allowed the presence of polar nematic and smectic phases. It was also shown that the additional dipole-dipole interaction does not influence these observations qualitatively [14, 15]. However, it should be noted that the Gay-Berne potential with a dipole at one end of the molecule leads to formation of the bilayer smectic phase [16]. Purely entropic systems constructed of pear-shaped molecules exhibit a cubic gyroid phase [17, 18]. Interestingly, this result is very sensitive to the details of the hard-core interaction. While this phase is observed for a pear described by two B’ezier curves using the hard pear Gaussian overlap model (PHGO), it vanished for the hard pears of revolution (HPR) model. Furthermore, in the first case, a bilayer smectic is also observed, while in the second model the authors reported isotropic and nematic phases [19].

![FIG. 1. (a) Family of wedges used in the study; they are built of six co-linear tangent spheres with diameters linearly from \( d \) to 1 (\( d \leq 1 \) is a parameter). (b) Wedge-shaped RM734 molecule known to form a polar nematic phase. Reprinted from Ref. [8] with the permission of RSC.](attachment:image.png)
carried out in the
Code availability
System snapshots were obtained numerically using the
ter one is a natural choice for purely steric repulsion.
Our model resembles the main features of the effective
shape of the RM734 molecule [Fig. 1(b)], for which
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\[ \text{II. METHODS} \]

A. Monte Carlo simulations

We assumed hard-core interactions between molecules to study entropic phase transitions in their systems. The equilibrium phases were classified as a function of the shape parameter \(d\) and the packing fraction \(\eta\). The latter one is a natural choice for purely steric repulsion. System snapshots were obtained numerically using the Monte Carlo scheme [24] using our RAMPACK software package (see Sect. Code availability). Integration was carried out in the \(NpT\) 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 \(\eta\). To allow relaxation of the full viscous stress tensor (including the shear part), we used a triclinic simulation box with periodic boundary condition. For a system of \(N\) particles, 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 \(\eta\). For a box move, the three vectors \(b_1, b_2, b_3\) that span the box were perturbed by small random vectors. The move was rejected if any overlaps were introduced. Otherwise, it was accepted ac-
cording to the Metropolis criterion with probability.

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

where \(\Delta V = (V - V_0)\) and \(V_0, V\) are, respectively, the volume of the box before and after the move. The perturbation ranges were adjusted during the thermal-
ization phase to achieve an acceptance probability of around 0.15. To accelerate simulations in a modern multi-threaded environment, we used domain decomposi-
tion technique [25] 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, prelimi-
inary simulations were performed by gradually compr-
ressing 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 \(9.5 \times 10^6\) full MC cycles and the production run with \(0.5 \times 10^6\) cycles to gather averages. The final snapshot of a run was used as a starting point for the next

\[ \text{with a slightly higher } p/T. \] Using the results as guidance, the main simulations were performed on a much larger system with \(N > 5000\) in a triclinic box. The initial config-
uration in the whole range of \(d\) was smectic A with \(\eta \approx 0.45\) (see Sec. III for the description of phases) pre-
pared 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 configu-
urations for each \(d\) were compressed under exponentially increasing pressure for \(3 \times 10^8\) 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 \(\hat{n}\) is detected by the average value \(\langle P_2(\hat{a} \cdot \hat{n}) \rangle\) of the second-order Legendre polynomial, where \(\hat{a}\) is the long axis of the molecule. Director \(\hat{n}\) can be inferred directly from the system using the second-rank \(Q\) tensor [20], which can be numerically computed as

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

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

Density modulation can be quantitatively described by the smectic order parameter \( \langle \tau \rangle \) \(^{[27]}\). It is defined as

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

where \( \mathbf{k} \) is the modulation wavevector compatible with PBC and \( \mathbf{r}_i \) is the center of the \( i \)th molecule. As the drift of the whole system is a Goldstone mode, the absolute value \( |\cdot| \) is taken before the ensemble averaging to eliminate it. All possible \( \mathbf{k} \) can be enumerated using reciprocal box vectors \( \mathbf{g}_1, \mathbf{g}_2, \mathbf{g}_3 \) \(^{[28]}\) and taking linear combinations of them with integer coefficients \( h, k, l \) (Miller indices \( [28] \)): \( \mathbf{k} = h \mathbf{g}_1 + k \mathbf{g}_2 + l \mathbf{g}_3 \). 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 \( \eta \), where molecules tend to form hcp-like structures. The local hexatic order can be measured using the so-called hexatic bond order parameter \( \langle \psi_6 \rangle \) \(^{[30]}\). For a two-dimensional system, it is defined as

\[
\langle \psi_6 \rangle = \frac{1}{N} \left\langle \sum_{i=1}^{N} \sum_{j=1}^{6} \exp(6i\phi_{ij}) \right\rangle,
\]

where \( \phi_{ij} \) is the angle between an arbitrary axis in the plane and the vector that joins the center of the \( i \)th particle 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 \( \langle \psi_6 \rangle \) 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. The first is a standard radial distribution function \( \langle \psi_6 \rangle \) \(^{[31]}\), which can be defined in a computationally friendly way as

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

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 \( \{\cdot\} \) and over independent snapshots \( \{\cdot\}_N \). 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 layer-wise radial distribution function in the direction orthogonal to \( \mathbf{k} \)

\[
\rho_{\perp}(r_{\perp}) = \frac{1}{n_L} \left\langle \sum_{i=1}^{n_L} \frac{dN_i (r_{\perp}, r_{\perp} + dr_{\perp})}{2\pi r_{\perp} dr_{\perp} \cdot (N/S)} \right\rangle_{N_i},
\]

where \( n_L \) is a number of layers, \( dN_i (r_{\perp}, r_{\perp} + dr_{\perp}) \) is the number of molecules in \( i \)th layer whose distance from a selected single molecule calculated along layer’s plane lies in the range \( (r_{\perp}, r_{\perp} + dr_{\perp}) \), and \( S \) is total surface area of all layers \( [32] \). In the end, it is averaged over all molecules in the layer \( \{\cdot\} \), all layers \( (1/n_L) \sum_{i=1}^{n_L} \{\cdot\}_i \), and uncorrelated system snapshots \( \{\cdot\}_N \).

As the results will show, the system develops a nontrivial polar metastructure. To quantify it, we use the layer-wise radial polarization correlation \( S_{\perp}^{110} \) \(^{[31]}\), defined alike \( \rho_{\perp}(r_{\perp}) \):

\[
S_{\perp}^{110}(r_{\perp}) = \frac{1}{n_L} \left\langle \sum_{i=1}^{n_L} (\hat{\mathbf{a}}_{ij} \cdot \hat{\mathbf{a}}_{ik})_{ijik} \right\rangle,
\]

where \( (\cdots)_{ijik} \) 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.

### III. RESULTS

Using the method described in Section 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), smectic A (SmA) and four crystalline phases: hexagonal crystal (Cr\(_{\text{hex}}\)), antiferroelectric splay crystal (Cr\(_{3S}\)Pa), antiferroelectric double splay crystal (Cr\(_{3D}\)Pa) and ferroelectric double splay crystal (Cr\(_{3D}\)Pf). The phase diagram is presented in Fig. 2 and order parameters are shown in Fig. 3. While Figs. 4, 5, 6 contain correlation functions. Moreover, representative equilibrium snapshots of all phases can be seen in Figs. 7, 8. The phases for all sampled pairs \( (d, \eta) \) were manually classified using order parameters and visual inspection of system snapshots. They are thoroughly analyzed in the following sections.
FIG. 2. Phase diagram of the system in $(d, \eta)$ space. The following liquid phases were recognized: isotropic (Iso), nematic (N) and smectic A (SmA) as well as crystalline ones: hexagonal crystal (Cr$_{hex}$), antiferroelectric double splay crystal (Cr$_{DS}P_A$), antiferroelectric splay crystal (Cr$_{SP}A$) and ferroelectric double splay crystal (Cr$_{DS}PF$). Black solid line at the top boundary of the phase diagram represents the maximal packing fraction $\eta$ for a given $d$ value.

A. Liquid phases

For the lowest packing densities $\eta$, an isotropic liquid is formed without long-range translational or orientational ordering. An example snapshot of this phase is shown in Fig. 7(a). It is characterized by almost zero values of nematic $\langle P^2 \rangle$ and smectic $\langle \tau \rangle$ and minimal value of $\langle \psi_6 \rangle$ (see Fig. 3). Radial distribution function [see Fig. 4(a)] also shows only local correlations that disappear for $r/\bar{d} > 4$, 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 $\bar{d}$: $r/\bar{d} = 1, 2, \ldots$, which can be attributed to the excluded volume effects.

Upon compression, for $d \in [0.5, 1]$ the nematic phase appears [see Fig. 7(b)], where molecules orient in a preferred direction called the director $\hat{n}$, retaining liquid-like centers’ positions. The nematic order parameter $\langle P^2 \rangle$ has a sharp jump on the phase boundary from 0 to 0.5-0.6 [Fig. 3(a)], while $\langle \tau \rangle$ and $\langle \psi_6 \rangle$ are still nearly minimal [Fig. 3(b, c)]. The range of the N phase in the packing fraction is around $\Delta \eta \approx 0.03$ for all $d$, however, it drops to 0 for the lowest values of $d$. Iso-N phase boundary reaches a minimal value of $\eta$: $\eta \approx 0.35$ for highest $d$ and moves upward to a triple point $(d, \eta) = (0.5, 0.4)$ when $d$ decreases. It is expected that, as with decreasing $d$, molecules become shorter (less anisotropic), and a higher pressure is needed to induce ordering. When $\eta$ increases, $\langle P^2 \rangle$ reaches 0.6-0.8. These values are quite high compared to a typical range in experiments [0.3, 0.7] [33], however, comparable to other hard shapes studied computationally [7, 20, 34]. The radial distribution function $\rho(r)$ [Fig. 4(b)] shows a series of maxima and minima around $r/\bar{d} = 1, 2, \ldots$ typical for liquids [24], however, compared to the Iso phase, the first maximum is over two times higher and correlations vanish later, for $r/\bar{d} > 6$. In

FIG. 3. Ensemble averages of observables as a function of the smallest sphere’s diameter $d$ and packing fraction $\eta$. (a) Nematic order $\langle P^2 \rangle$, (b) smectic order $\langle \tau \rangle$, (c) local hexatic order $\langle \psi_6 \rangle$. 

FIG. 4. (a) Radial distribution function $\rho(r)$ [Fig. 3(b)] shows a series of maxima and minima around $r/\bar{d} = 1, 2, \ldots$ typical for liquids [24], however, compared to the Iso phase, the first maximum is over two times higher and correlations vanish later, for $r/\bar{d} > 6$. In
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 $[(d, \eta) = (0.5, 0.46)]$, (d) Cr$_{hex}$ $[(d, \eta) = (0.95, 0.51)]$ phases. Distance $r$ is scaled by the average diameter of balls in the molecule $d = (d + 1)/2$. Correlation peaks are clipped on panels (c) and (d), however their values are shown inside the plots.

FIG. 5. Layer-wise 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$_{DS}$P$_A$ $[(d, \eta) = (0.75, 0.52)]$, (d) Cr$_{DS}$P$_F$ $[(d, \eta) = (0.6, 0.51)]$ and (e) Cr$_{SP}$A $[(d, \eta) = (0.9, 0.68)]$ phases. Moreover, panel (f) shows magnification of a part of panel (b). Distance $r_{\perp}$ is scaled by the average diameter of balls in the molecule $d = (d + 1)/2$. Correlation peaks are clipped on panels (b), (c) and (d), however their values are shown inside the plots.

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, $S_{11}^{10}(r_{\perp})$ can still be computed by defining them in an arbitrary way. The results are presented in Fig. 5(a). Clearly, polarization correlations are minor and very short-ranged, vanishing completely for $r_{\perp} > 2d$.

Type A smectic phase (SmA) is formed over the Iso phase for $r \in [0.4, 0.5]$ and over the N phase for $r \in [0.5, 1.0]$, characterized by a prominent jump of smectic order $\langle \psi \rangle$ [Fig. 3(b)] to around 0.5 and visible formation of layers [cf. snapshot from Fig. 3(c)]. The director $\hat{n}$ is parallel to the smectic wavevector $\mathbf{k}$. One can observe a slight increase in the value of the parameter $\langle \psi \rangle$ from 0.38 to 0.45 compared to the Iso and N phases, and it reaches 0.6-0.65 for the high $\eta$ regime of this phase, which means that there is some degree of local hexatic ordering. Nevertheless, a long-range bond order is not present (in contrast to, for example, type B smectic [55]). Nematic order $\langle P_2 \rangle$ grows with increasing $\eta$ up to nearly 1, however it has no sudden jump on N-SmA boundary. Similarly, for the N phase, the boundary moves upward with decreasing $d$, which can again be explained by a lower anisotropy of the molecules. Radial distribution function $\rho(r)$ [see Fig. 4(c)] has a more complex structure than for the Iso and N phases. There are two superimposed sequences of minima and maxima. In the first sequence covering the whole studied range of $r/d$ maxima appear for $r/d \approx 7, 14$. They correspond to the distances between the strata. The second sequence has a spacing around $d$ and vanishes for $r/d > 6$. Its first maximum is very sharp; it reaches $\rho(r) = 6.7$. This sequence corresponds to a short-range order of molecules within the layers. It is confirmed by looking at layer-wise $\rho_{\perp}(r_{\perp})$ [Fig. 5(a)], where the correlations between the layers are phased out. There, maxima appear for $r_{\perp}/d = 1, 2, \ldots$ and vanish completely for $r_{\perp}/d > 9$. Thus, the translational order is only local. Lastly, likewise for the nematic phase, there is no global correlation of molecular polarization vectors, as indicated by the $S_{11}^{10}(r_{\perp})$ correlation function [see Fig. 4(b)]. For $r_{\perp}/d \approx 1$ slight anticorrelation $[S_{11}^{10}(r_{\perp}) < 0]$ is visible due to entropic reasons – close molecules tend to orient in opposite ways to increase packing density. The correlations vanish for $r_{\perp}/d > 4$. 
Over $\eta \approx 0.5$ four distinct types of hexagonally ordered solids retaining SmA layered structure appear. For $d \in [0.75, 1.0]$, SmA is adjacent to a hexagonal non-polar crystal phase denoted Cr$_{\text{hex}}$, whose snapshot is presented in Fig. 3(a). Both $\left< P_2 \right>$ and $\langle \tau \rangle$ are equal to almost 1 in the entire range [Fig. 3(a), b]). There is also a sharp jump in the local hexatic order parameter $\langle \hat{n} \cdot \hat{n} \rangle$ confirming (locally) hexatic structure within a layer. The presence of long-range translational order becomes apparent when one refers to the radial and layer-wise pair distribution function $\rho(r)$, $\rho_{\perp}(r_{\perp})$ [Figs. 4(d), 5(b)]. For $\rho(r)$, we observe two sequences of maxima. Similarly to SmA, the first one with larger spacing corresponds to layering, and the second one with a smaller peak-to-peak distance corresponds to inter-layer order. However, contrary to SmA, the second sequence does not vanish quickly and extends throughout the entire plotted range of $r_{\perp}/d$. $\rho_{\perp}(r_{\perp})$ also shows long-range correlations. Furthermore, the structure of the first few peaks of $\rho_{\perp}(r_{\perp})$ [see Fig. 5(f)] agrees with the one observed for the hexagonal honeycomb lattice, see eg. Fig. 3 in Ref. [46]. As shown by the $S_{\perp}^{110}(r_{\perp})$ correlations [Fig. 5(c)], the polarization order is weak and extremely short-range, disappearing already for $r_{\perp}/d > 2$.

For $d = 1$, the wedge reduces to a well-known linear tangent hard-sphere (LTHS) hexamer. Equilibrium phases in the LTHS model were the subject of, e.g. Ref. [20]. Trivially, the ground state configuration is given by a close pack of spheres [47] and has packing fraction $\eta = \pi/\sqrt{18} = 0.74 \ldots$. Here, we were able to reach $\eta \approx 0.73$ upon compression, which is in a good agreement which the exact value taking into account the presence of a small number of defects in the Monte Carlo configuration. There are many ways of arranging LTHS chains into a close packed configuration. The obvious choice is to form fcc or hcp layers of molecules with a 30$^\circ$ tilt (cf. CP$_1$ lattice in Ref. [48], also used in the previous mentioned Ref. [20]). However, those configurations are unlikely to form on the compression route from SmA layers. More probable are non-tilted variants with a (partial) hexatic order. We identified two such structures denoted as fcc$_B$ and hcp$_B$ (see Appendix A), where 6 nearest neighbors within a layer form slightly deformed regular hexagons. This deformation correlates well with values of $\langle P_2 \rangle$ below 0.8 for $d = 1$ compared to over 0.8 for $d = 0.85$. In the fcc$_B$ and hcp$_B$ lattices, polymers

Both sequences of phase transitions displayed by the system

1. Iso $\leftrightarrow$ N $\leftrightarrow$ SmA

2. Iso $\leftrightarrow$ SmA

are prominent and well recognized in systems of elongated molecules, both in computational studies [6] [7] [20] [34], and in experiments [36] [38], although the second sequence is less common in physical systems. However, for asymmetric molecules, modulated phases may be formed. They can be analyzed using the Oseen-Zocher-Frank free energy [39] [41]

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

where subsequent terms correspond to splay, twist, and bend deformations. Usually, all $K_{ij}$ constants are positive, and the ground state is an ordinary nematic. However, for particular shapes of molecules, some of these constants may become negative, and lack of modulation is no longer favored energetically. For example, for banana-shaped molecules, where $K_{33}$ bend constant falls below 0, twist-bent and splay-bent phases are observed [5] [6] [12]. For wedges, on the other hand, the $K_{11}$ splay constant can become negative [13] leading to the formation of polar splay nematic and smectic phases [44] [45]. However, in our model, no modulated or polar liquid phases were recognized. Second-virial bifurcation analysis (see Appendix B) of N-N$_P$ phase transition also confirmed its absence. There are two possible culprits: the first is the moderate length of the molecule and the second is the concavities between the beads.
FIG. 7. 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. First column presents the top view of the snapshot \((xy)\) plane, while the second one the side view \((xz)\) plane in a way that 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 \(\hat{a}_i\) with respect to the global director \(\hat{n}\) as per first order Legendre polynomial \(P_1(\hat{a}_i \cdot \hat{n}) = \hat{a}_i \cdot \hat{n}\), allowing one to discern opposite polarizations. In the third column molecules’ centers are marked as black dots, and the simulation box is oriented in the same way as the second column (side view).

form infinite columns that can be translated by integer multiples of the diameter \(d = 1\) of the mers. A slight off-layer spread can be seen in our results [see the last column in Fig. 8(a)], which also lowers the value of \(\langle \tau \rangle\).

When \(d\) is decreased and the variation of beads’ diameters grows, a closed-packed configuration ceases to be preferred and polar blue phases emerge. The first is visible in a range around \(d = 0.85-0.95\) (see Fig. 2). The snapshot is presented in Fig. 8(b). As clearly visible, within each layer clusters with macroscopic polarization spontaneously emerge and arrange in a striped metastructure. Two neighboring clusters have opposite
FIG. 8. System snapshots of all crystalline phases in the system. Rows correspond to, respectively, (a) Cr$_{hcp}$ \([(d, \eta) = (0.95, 0.51)]\), (b) Cr$_{SP}$ \([(d, \eta) = (0.9, 0.68)]\), (c) Cr$_{DS_P}$ \([(d, \eta) = (0.75, 0.52)]\) and (d) Cr$_{DS_P}$ \([(d, \eta) = (0.6, 0.51)]\) phases. Columns’ order and color coding are the same as in Fig. 7.
polarization and are separated by planar defects in a polarization field. Molecules within a cluster have a long-range hexatic order, as indicated by a high value of $<\psi_0>$ [Fig. 3(c)] and the correlation function $\rho_s(r_{\perp})$ [Fig. 3(e)]. Density correlations have a very complicated structure. Firstly, there is a series of wide maxima and minima separated by $\Delta r_{\perp} \approx 6d$, which corresponds to the width of stripes. Around those short, wide maxima there are 3-4 sharper ones separated by $\Delta r_{\perp} \approx d$. They correspond to correlations between particular rows of shapes across the stripes. On top of it there are numerous small maxima, which are correlations between individual beads in a highly regular lattice (the phase appears only for very high $\eta$ values close to the maximal packing). Macroscopic polarization of the cluster is confirmed by $S^{110}_{\perp}(r_{\perp})$ correlations [see Fig. 6(d)]. Likewise for $\rho_s(r_{\perp})$, we see minima and maxima, however with two times smaller separation, as the adjacent stripes have opposite polarizations. On top of it, there is a similar series of additional maxima as in $\rho_s(r_{\perp})$. The nematic order ($P_2$) remains above 0.8, however, is slightly lower than for Cr$_{hex}$. The reason becomes clear when we notice that clusters have the splay modulation in polarization field, namely, it is parallel to the director in the middle of the stripe and gradually leans when one moves towards the boundary. On the other hand, the preferred direction does not change along the length of a stripe. Two dimensional splay modulation helps to fill the space more efficiently and is inherently related to the shape of the wedge, which is reflected in a lower value of the elastic constant $K_{11}$. Notably, clusters in adjacent layers continue the pattern; however, their polarization has always an opposite sign.

The same applies to the direction of splay modulation. As a result, the stripes ($y$-axis columns) are arranged in a two-dimensional checkerboard pattern. The largest and smallest balls that build molecules form hexagonal lattices with different lattice constants, and thus the polarization switch in a neighboring layer enables a more compatible arrangement of adjacent layers. To capture the most important properties of the structure, we call it antiferroelectric splay crystal – Cr$_A$. The term antiferroelectric refers to opposite polarization of the clusters in adjacent layers. Notably, Cr$_A$ phase appears even very close to $d = 1$, however the phase boundary increases dramatically with growing $d$. The reason is that higher densities are required to induce polar order when the gradient of the balls’ diameters is smaller. In particular, in the whole range the system crystallizes first into a structure Cr$_{hex}$, which is then followed by a transition to Cr$_A$, thus SmA-Cr$_A$ phase transition is not present.

Another polar phase is formed above Cr$_{hex}$ for $0.75 \leq d \leq 0.8$. Its snapshot is presented in Fig. 3(c). Once again, polarization clusters are formed. However, they organize within a layer into a checkerboard pattern instead of stripes, where each square domain is neighboring four domains with an opposite polarization. When one moves to an adjacent layer, clusters’ polarizations are flipped, likewise for Cr$_A$, which means, that the checkerboard pattern is actually three dimensional. Splay pattern also changes. It is now three dimensional – the sense of splay vector $\hat{n}(\nabla \cdot \hat{n})$ correlates with the one of the polarization field. The particles are parallel to the $z$-axis in the middle of the cluster and they gradually lean when the distance from the center is increased. We call this structure antiferroelectric double splay crystal – Cr$_{DS}$. It is important to note, that the magnitude of splay vector in the double splay structure is higher than for a single splay (assuming the same maximal curvature). It helps to understand the origin of Cr$_A$-Cr$_{DS}$ transition – splay deformation is promoted stronger for particles with a smaller value of $d$, which facilitated higher modulation of the direction field realized by the checkerboard pattern. It is reflected in a slightly lower value of $\langle P_2 \rangle$ compared to Cr$_A$. Transversal density correlation $\rho_s(r_{\perp})$ [Fig. 3(c)] is similar as for Cr$_{hex}$ [Fig. 3(b)], with, however, slightly higher damping. Polarization correlation function $S^{110}_{\perp}(r_{\perp})$ [Fig. 3(e)] shows positive correlations up to $r_{\perp} \approx 6.5d$ and negative correlations up to $r_{\perp} \approx 13d$, which, in line with Fig. 8(c), approximates the cluster radius as $(6-7)d$.

For $d < 0.75$ the third frustrated polar structure is formed directly over SmA. Likewise for Cr$_{DS}$, we observe the emergence of polar clusters, again arranged in a checkerboard pattern [cf. Fig. 3(d)]. However, instead of alternating between neighboring layers, cluster form $z$-axis columns stretching throughout the whole height of the simulation box; thus we shall call the phase ferroelectric double splay crystal – Cr$_{DS}$P$_F$. This is accompanied by bending of layers, as visible in the second and third panels of Fig. 8(d), also shown by the smectic order ($\tau$) dropping to 0.4-0.7. For the same reason $<\psi_0>$ is lowered to 0.65-0.75 – orthogonal projection of the structure within a curved layer deforms the hexatic arrangement. Weaker nematic order ($P_2$) in the range 0.5-0.8 is in line with a visibly large splay modulation. As we shall discuss, layer bend and ferroelectric arrangement are mutually correlated. In Cr$_A$ and Cr$_{DS}$ the opposite interlayer polarization allowed the compatible hexagonal beads lattices to be adjacent. However, it forced the layers to be flat. There is another way of efficient packing, where clusters are fragments of a spherical shell. However, this requires a ferroelectric arrangement in the direction of $k$ to match the signs of curvatures, sacrificing the compatibility of the beads’ lattice constants. Cr$_{DS}$P$_A$ transitions into Cr$_{DS}$P$_F$ where the latter trade-off leads to higher packing densities. The packing microstructure is similar to Cr$_{DS}$P$_A$. There are long-range correlations of $\rho_s(r_{\perp})$ [Fig. 3(d)], which, however, vanish faster than for Cr$_{DS}$P$_A$ or Cr$_{hex}$. It can be attributed to more irregular domain walls, which implicate weaker correlations between adjacent clusters. $S^{110}_{\perp}(r_{\perp})$ [Fig. 3(f)] is similar to Cr$_{DS}$P$_A$; cluster radius estimated at 7-8 molecule diameters agrees with a visual inspection of Fig. 8(d).
With decreasing $d$ the variation of ball diameters grows larger, which hinders the optimal filling of the space. As a result, estimated maximal packing fraction $\eta$ (see black solid line in Fig. 2) falls monotonically with $d$ reaching $\eta \approx 0.61$ for $d = 0.4$.

IV. SUMMARY

Using Monte Carlo simulation, we have computationally obtained and analyzed the phase diagram for a system made up of hard wedge-shaped molecules composed of tangent spheres. For packing fractions below $\eta \approx 0.5$, corresponding to the liquid phase, we observed isotropic (Iso), nematic (N), and smectic A (SmA), expected for systems built with calamitic molecules. We have not observed polar nematic or (splay) smectic phases. For $\eta$ greater than 0.5, the system crystallizes and forms one of four distinct phases in different regions of $(d, \eta)$. For $d \geq 0.75$, when the molecule is not far from the LHTS hexamer, SmA transforms to a standard non-polar hexagonal crystal (Cr$_{\text{hex}}$). However, for all $0.75 \leq d < 1$ further compression produces two another crystalline phase that will have a frustrated polar order with splay modulation. For $0.75 \leq d \leq 0.8$ three-dimensional checkerboard mesostructure, called the antiferroelectric double splay crystal (Cr$_{\text{DS}}$P$_A$) is formed, while for $d \geq 0.85$ striped antiferroelectric splay crystal (Cr$_{\text{A}}$P$_A$) phase emerges. For $d < 0.75$, SmA transforms directly into another frustrated polar phase, called ferroelectric splay crystal (Cr$_{\text{S}}$)P$_A$, where the polarization clusters form long columns. To our knowledge, these structures were not previously observed, but theoretical arguments support the existence of such mesophases [49].

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 RAMPACK simulation package used to perform Monte Carlo sampling is available at [https://github.com/PKua007/rampack](https://github.com/PKua007/rampack)

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Appendix A: Non-tilted hexagonal configurations in a close packing of LTHS polymers

![Hexagonal configurations](image)

FIG. 9. (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.

We want to establish how one can arrange maximally packed LTHS polymers assuming that they form hexatic layers without a tilt (long molecular axes should be perpendicular to layers). A naive approach would be to prepare hexagonal honeycomb layers and stack them as in the type B crystal [50], which occurs, for example, in a system of spherocylinders [3, 54]. However, this configuration is not maximal. Thus, we have to soften two conditions: molecules can be slightly off-layer and hexagons can be slightly deformed. We identified two such configurations, based on fcc and hcp lattices.

The first is constructed from an fcc lattice of spheres [see Fig. 9(a)]. For polymers with $k$ beads of diameter $d$, the unit cell has dimensions $d \times d\sqrt{2} \times kd$ and two molecules with geometric centers: $(0, 0, kd/2 - d/4)$ and $(d/2, \sqrt{2}/2, kd/2 + d/4)$. We denote this configuration as fcc$_B$.

The second is based on the hcp lattice [see Fig. 9(b)]. The unit cell has dimensions $d\sqrt{3} \times 2d\sqrt{3}/3 \times kd$ and 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 call this structure hcp$_B$. 
Appendix B: Structure analysis using Density Functional Theory

Here, we analyze the stability of some of the structures obtained in simulations using the second-virial Density Functional Theory corrected by the Parsons-Lee term (DFTPL) [51,55]. Within this approach, we seek to gain more information about the tendency of wedge-shaped molecules to generate (at least metastable) long-range ferroelectric order. The use of the DFTPL approach proved especially useful in the analysis of stable structures for hard molecules of complex shapes (see e.g. [5]). We start with a brief summary of DFTPL theory for hard uniaxial particles. More details can be found in e.g. in [5] [51,55]. According to this theory, the Helmholtz free energy $F$ of a system of $N$ particles in volume $V$ at temperature $T$ is a functional of the single particle probability density distribution function $P(X_i)$, where $X_i \equiv \{x_i, \hat{a}_i\}$ represents the position and orientation of the $i$-th molecule. The distribution $P(X_i)$ is normalized so that

$$Tr(X_i)P(X_i) = 1, \quad Tr(X_i) = \int_V d^3r_i \int d^2\hat{a}_i.$$  

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

$$f(P) = \frac{F[P]}{Nk_B T} = Tr[X_f \ln P(X)] + C(\eta) \frac{\bar{\rho}}{2} Tr[P(X)H_{\text{eff}}(X_i[P]) + ...,$$  

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

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

where $\xi(\cdot)$ is the contact distance between two particles, $\Theta(\cdot)$ is the $\Theta$-Heaviside function and $k_B$ is the Boltzmann constant. The factor $C(\eta) = (1/4) \frac{4-3\eta}{(1-\eta)^2}$ renormalizes second-order virial expansion [51] to account for higher-order terms [52,53]. Additionally, $r_{12}$ is the distance between two particles, $\eta = \frac{v_{\text{mol}} N}{v_{\text{mol}} \bar{\rho}}$ is the packing fraction, and $v_{\text{mol}}$ is the volume of a molecule.

The equilibrium states correspond to the minimum of the free energy functional, Eq. (B2), with respect to $P(X)$, subject to the normalization condition, Eq. (B1). The procedure is equivalent to solving the self-consistent integral equation

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

where

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

for stationary distributions $P_s(X)$ and selecting the one that minimizes the free energy $\text{[B2]}$ for a given set of control parameters. Generally, for wedge-shaped molecules, a question of interest is whether they can stabilize states with long-range polar order, such as polar nematics or smectics. The effective method to explore this problem is the bifurcation analysis of Eq. (B2) about the reference state, which is usually the isotropic or uniaxial nematic phase. Since for wedges the steric dipoles orient, on average, parallel to the director $\hat{n}(r)$, various local polar orderings of predefined polarization profile $\hat{p}(r)$ ($|\hat{p}(r)| = 1$, $\hat{n}(r) = \pm \hat{p}(r)$), can be tested against destabilization of that reference state.

Here we limit ourselves to bifurcation studies from the reference uniaxial nematic phase. Additionally, since simulations indicate that the nematic order is high both in the uniaxial nematic and at the transition from the uniaxial nematic to higher ordered phases (see Fig. (2)), we simplify the analysis by assuming that the orientational degrees of freedom of $i$-th polar molecule are just reduced to two states: parallel ($s_i = 1$) and antiparallel ($s_i = -1$) to the locally preferred orientational ordering:

$$a_i = s_i \hat{p}(r_i).$$  

Hence,

$$Tr(X_i) \equiv Tr(r_i,s_i) = \int_V d^3r_i \sum_{s_i=\pm1}.$$  

In practical calculations, we model the distribution function $P(r, s)$ by decomposing this into the conditional probability $P(r, s)$ of finding the center of mass of a molecule in $r$ times the conditional probability $P(s/r)$ of finding a molecule oriented at $s$ given $r$

$$P(r, s) = P(r)P(s/r) \approx P(r)P(s/\hat{p}(r)).$$  

where

$$Tr[P(r)] = 1 \quad \text{and} \quad Tr[P(s/r)] = 1, \quad \forall r \in V,$$  

Hence, for a given model field $\hat{p}(r)$ we can take

$$P(s/\hat{p}(r)) = \frac{1}{2}(1 + \langle s \rangle s),$$  

where

$$\langle s \rangle = Tr[s \hat{p}(r)].$$  

is the order parameter that describes the mean polar arrangement of the particles and where $\langle s \rangle \hat{p}(r)$ plays the role of the average local polarization. Additionally

$$P(r) = \frac{1}{V} (1 + n_\tau \langle \tau \rangle \tau(r) + ...),$$  

where

$$\langle \tau \rangle = Tr[\tau(r)P(r)].$$
is the leading order parameter responsible for the smectic or crystalline ordering, and \( n_r \) is the normalizing factor. For example, in the case of smectics with density modulation along the \( z \) axis of the laboratory frame \( \tau(\mathbf{r}) = \cos(2\pi z/d) \) and \( n_r = 2 \), where \( d \) is the structure period. Additionally, the length of the box \( (V)^{\frac{1}{3}} \) is assumed to be a multiple of \( d \).

Calculations can now proceed by noting that \( \langle s \rangle \) and \( \langle \tau \rangle \) are small near the bifurcation point. This permits us to linearize the Eq. (B14) about \( \langle s \rangle = \langle \tau \rangle = 0 \) and solve the resulting equation/s for \( \eta = \eta_b \). The most probable structure that can stabilize as a result of the phase transition from the uniaxial nematic would usually be the one that leads to a minimal \( \eta_b \).

As an example, we test whether our molecules can stabilize a uniaxial polar nematic \( (\tau(\mathbf{r}) = 0, \hat{p}(\mathbf{r}) = \hat{p}_u) \) due to purely excluded volume interactions. In this case the Eq. (B14) reduces to

\[
P(s_1) = Z^{-1} e^{-\eta C(\eta) T_{\langle s \rangle}} \frac{\Theta_{\text{ex}}(s_1, s_2) P(s_2)}{\Theta_{\text{ex}}(s_1, s_2) P(s_2)} \quad \text{(B14)}
\]

where

\[
\Theta_{\text{ex}}(s_1, s_2) = T_{\langle r_{12} \rangle} \left[ \frac{\Theta_{\text{ex}}(s_1, s_2) - r_{12}}{v_{\text{mol}}} \right] \quad \text{(B15)}
\]

is the reduced excluded volume for a given orientation of particles, and where \( P(s) \equiv P(s/\hat{p}_u) \). Introducing the parameterization, Eq. (B10), and observing that

\[
\Theta_{\text{ex}}(s_1, s_2) = \Theta_{\text{ex}}(s_1 s_2) = \Theta_0 - s_1 s_2 \Theta_{\tau}, \quad \text{(B17)}
\]

where

\[
\Theta_0 = \frac{1}{2} \left[ \Theta_{\text{ex}}(1, 1) + \Theta_{\text{ex}}(1, -1) \right] \quad \text{(B18)}
\]

\[
\Theta_{\tau} = \frac{1}{2} \left[ \Theta_{\text{ex}}(1, -1) - \Theta_{\text{ex}}(1, 1) \right] \quad \text{(B19)}
\]

we get an Ising-like mean-field equation for \( \langle s \rangle \)

\[
\langle s \rangle = \text{tanh}[(\langle s \rangle)\eta C(\eta) \Theta_{\tau}], \quad \text{(B20)}
\]

Note that the reference uniaxial nematic phase \( \langle s \rangle = 0 \) is always the solution of Eq. (B20). After the linearization of the Eq. (B20) about small nonzero value of \( \langle s \rangle \) we obtain a homogeneous equation for \( \langle s \rangle \)

\[
\langle s \rangle = \langle s \rangle \eta C(\eta) \Theta_{\tau}, \quad \text{(B21)}
\]

which leads to a nonzero solution at \( \eta = \eta_b \), where \( \eta_b \) satisfies the equation

\[
1 = \eta_b C(\eta_b) \Theta_{\tau}. \quad \text{(B22)}
\]

Hence, the nonzero solution for \( \langle s \rangle \) bifurcates from \( \langle s \rangle = 0 \) at \( \eta_b \), given \( \eta_b > 0 \), and becomes the solution of the full equation (B20) for \( \eta > \eta_b \). Unfortunately, in our case \( \eta_b < 0 \), which makes the ferroelectric polar nematic order unstable. We conclude that, within the assumptions and simplifications adopted, the density functional theory does not predict the existence of global polar nematic ordering in the studied system.

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