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Nematic stability of discotic liquid crystals with orientation-dependent interactions

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Technological applications of discotic nematogens are limited by the robustness of the columnar phases. This investigation employs Monte Carlo simulations to explore the potentiality of tailoring specific interactions of either stacking or peripheral type in order to enhance nematic stability. It is concluded that the nematic phase is favored for discotic particles systems with homogeneous or weakly directional interactions. However, a substantial increase in the directionality of the interaction (stacking or edge-to-edge) leads systematically to a suppression of the nematic domains in favor of the columnar phases.

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Discotic liquid crystals stand as promising materials for numerous technological applications [1–5]. The current relevance of discotics is illustrated in recent reviews [4,5] and reference textbooks [6–8]. The bulk of the technological applications of discotic liquid crystals relies on the specific properties of their columnar phases. On the other hand, studies about the potential applications of the discotic nematic phase are more scarce in spite of the recognized potential of their optical and electronic properties [3,9,10]. A fundamental aspect is that whereas columnar phases are in general robust in discotic materials, stable nematic phases are more difficult to obtain. This is in contrast with the calamitic rodlike mesogens, where the nematic phase is common [11]. Hence, the development of novel applications of discotic nematogens will benefit from computational predictions about the fundamental molecular or colloidal properties promoting the discotic nematic phase, ideally over a broad range of thermodynamic parameters.

The main aim of the present work is to explore the potential of tailoring the molecular interactions in discotic systems to tune the columnar-nematic-isotropic phase equilibrium in particles of moderate asymmetry. Very recently, new tools have been developed for the computer simulation of disklike spherocylinder model particles incorporating different kinds of dispersive interactions [14]. This approach is particularly appealing as it allows for the systematic coarse-grained modelization of molecular attributes, beyond shape, that might have an influence on the phase behavior (e.g., the incorporation of specific functional groups at particular positions of the molecular structure). We report here on a study for spherocylinder particles with aspect ratio $L/D=0.1$ [12,13]. For this aspect ratio the steric effects alone lead to a stable nematic phase in the oblate hard spherocylinder fluid (OHSC) fluid. Our goal then is to clarify whether dispersive interactions with specific orientational features may be cooperative with the steric forces and further broaden the nematic phase regime.

The interaction models employed in the study are built from different parametrizations of the recently proposed Oblate Gay-Berne-Kihara (OGBK) potential [15–17]. The OGBK model extends the original Kihara spherocylinder potential [18] by incorporating an explicit dependence of the interaction strength on the relative orientation of the particles, without distorting the spherocylinder geometry. Table I lists the triads of parameters (κ', ν, μ) used in the present study. These parameters control the relative energies of pair configurations with different relative orientations, as explicitly outlined in Ref. [15]. It can be noted that $\kappa' > 1$ favors stacked configurations, whereas $\kappa' < 1$ leads to stronger attractions for peripheral side-side approaches. Hence, in the present study the models OGBK(2,1,1) and OGBK(5,2,1) display a strongest interaction for stacked configurations, while for the models OGBK(0.2,1,1), OGBK(0.1,1.5,2), and OGBK(0.2,2,1) the intermolecular interaction is more intense in the edge-to-edge configurations. The notation OGBK(κ', ν, μ) has been applied above and throughout the text. In addition, the discotic 12–6 Kihara model (OKIH) is included in the study. This latter model assigns the same Lennard-Jones-type potential to all types of pair orientations and can be considered as a particular case of the OGBK model with $\kappa'=1$ and $\mu=0$.

The liquid crystal phase diagram for each model was determined by means of a systematic Monte Carlo study in the Isobaric-Isothermal ensemble. The simulation method is outlined in detail in Ref. [15]. For the present study, the simulation was started from a hexatic columnar arrangement that was equilibrated to a columnar disordered D_{hd} phase. Such

TABLE I. Minimum interaction energies per molecule (well depths), $U^*=U/\epsilon$, of pairs of particles in selected parallel and perpendicular configurations for the different $L/D=0.1$ discotic spherocylinder models OGBK(κ', ν, μ). Note that ϵ corresponds to the well depth of the discotic Kihara model, 12–6 OKIH and of the OGBK model for crossed configuration (—O).

Interaction model	Stacked ‖	Edge-edge — —	T-shape —|	Crossed —O
12–6 OKIH	−1.00	−1.00	−1.00	−1.00
OGBK(2,1,1)	−10.0	−5.02	−1.33	−1.00
OGBK(5,1,1)	−25.1	−5.02	−1.66	−1.00
OGBK(0.2,1,1)	−1.00	−5.02	−0.33	−1.00
OGBK(0.1,1.5,2)	−1.13	−11.3	−0.23	−1.00
OGBK(0.2,2,1)	−5.08	−25.4	−0.33	−1.00

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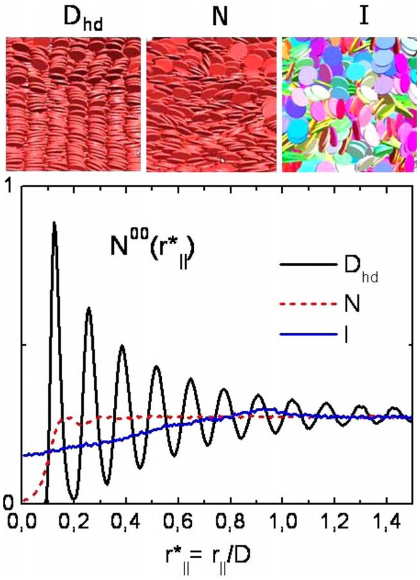

FIG. 1. (Color online) Typical snapshots and particle correlation functions along the nematic director in the columnar D_{hd}, nematic and isotropic phases of the discotic OGBK fluids with $L^*=0.1$.

columnar phase was then slowly melted to the nematic phase (if present) and finally to the isotropic phase. The only exception to this procedure was the OGBK(0.2,2,1) model which at low temperature equilibrated in the crystalline interdigitated D_{hi} phase [14] and melted directly to the isotropic phase upon heating. Figure 1 illustrates part of the structural information used to establish the phase diagram (an extended description can be found in Refs. [14,15]). The distribution function $N^{00}(r_{\|})$ reflects the pair correlations along the nematic director of the fluid ($r_{\|}$ denotes the projection of the pair distance vector on the nematic director; only particles with the complementary perpendicular projection $r_{\perp}$ smaller than the particle diameter are considered [14]). Structure in $N^{00}(r_{\|})$ is associated with columnar organization of the fluid, as can be appreciated in the snapshots included in Fig. 1.

Table II and Fig. 2 characterize the boundary states of the columnar-nematic, columnar-isotropic, and nematic-isotropic transitions of the OGBK models investigated. The previous results for the OHSC model [14] have also been included for comparison. A first quantitative effect that can be observed is an overall increase in the temperature of the transitions as the pair interaction potential becomes greater. This trend is appreciated in going from the OHSC and OKIH fluids to the OGBK models with growing attractions in the upper panel of Fig. 2. Such behavior is expected if functional groups of increasingly active interactions are incorporated to a given discotic molecular architecture.

A more relevant finding in the context of the present work is the decreasing range of stability of the nematic phase when

TABLE II. Characterization of the columnar-nematic-isotropic boundary states for the OHSC, OKIH, and OGBK(κ', ν, μ) fluids. The reduced temperature, $T^{\dagger}=k_BT/\epsilon$ (k_B denotes the Boltzmann constant), density, $\rho^*=\rho D^3$, and internal energy per molecule, $U^*=U/\epsilon$, are indicated. The reduced pressure was set to $P^{\dagger}=PD^3/\epsilon=100$. For the OHSC model the listed values of $T^{\dagger}$ have been obtained from the relevant ratio $P^*=PD^3/k_BT=P^{\dagger}/T^{\dagger}$ employed in the simulations [14].

Model		Columnar/nematic	Nematic/isotropic	Columnar/isotropic
OHSC	$T^{\dagger}$	1.59/1.61	3.13/3.23	
	ρ^*	5.98(1)/5.54(1)	4.05(1)/3.86(1)	
	U^*	0.00/0.00	0.00/0.00	
12–6 OKIH	$T^{\dagger}$	1.45/1.50	3.30/3.35	
	ρ^*	6.40(1)/6.07(1)	4.17(1)/4.08(1)	
	U^*	−2.36(4)/−2.33(4)	−1.13(3)/−1.11(2)	
OGBK(2,1,1)	$T^{\dagger}$	3.60/3.65	4.65/4.70	
	ρ^*	7.65(1)/4.90(1)	3.82(1)/3.64(1)	
	U^*	−22.0(4)/−8.20(4)	−4.28(3)/−3.63(2)	
OGBK(5,1,1)	$T^{\dagger}$			4.85/4.90
	ρ^*			6.83(2)/3.77(2)
	U^*			−26.6(4)/−7.06(4)
OGBK(0.2,1,1)	$T^{\dagger}$	2.95/3.00	4.75/4.80	
	ρ^*	8.29(1)/5.67(1)	3.53(1)/3.45(1)	
	U^*	−17.9(4)/−10.3(4)	−1.92(3)/−1.65(2)	
OGBK(0.1,1.5,2)	$T^{\dagger}$	5.70/5.75	6.10/6.15	
	ρ^*	8.48(1)/4.49(1)	3.64(1)/3.11(1)	
	U^*	−41.5(4)/−13.8(4)	−6.67(3)/−2.48(2)	
OGBK(0.2,2,1)	$T^{\dagger}$			11.5/11.8
	ρ^*			8.73(2)/2.21(2)
	U^*			−105.5(4)/−1.87(4)

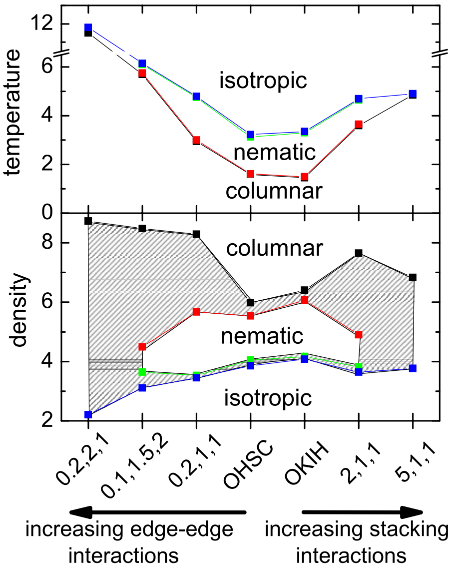

FIG. 2. (Color online) Schematic representation of the columnar–nematic–isotropic reduced temperatures (top) and densities (bottom) ($T^{\dagger}=k_BT/\epsilon$ and $\rho^{*}=\rho D^3$, respectively) at the phase boundaries of the OGBK(κ', ν, μ) models (the three parameters are indicated in the axis labels). Note that the nematic phase becomes less stable in favor of the columnar phase if strongly directional pair interactions are incorporated to the particles.

the directionality in the interaction becomes sufficiently strong. This effect is found when either the stacked interaction or the edge-edge interactions are enhanced, as illustrated in Fig. 2. The homogeneous soft attractive well of the 12–6 OKIH model increases slightly the density domain of stability of the nematic phase. Interestingly, the moderate increase in the side-to-side interactions introduced in the OGBK(0.2,1,1) model also keeps the nematic phase stable and even broadens its domain with respect to the OHSC and OKIH fluids. However, if the side-to-side interactions become too strong, the range of stability of the nematic phases shrinks appreciably, as in the OGBK(0.1,1.5,2) fluid, or vanishes completely leading to a columnar-isotropic transition, as found for the OGBK(0.2,2,1) fluid. Moreover, if stacking interactions of even moderate magnitude are introduced in the discotic particles, as in the OGBK(2,1,1) model, the range of stability of the nematic phases is already significantly reduced in comparison to the OHSC and OKIH fluids. For stronger stacking attractions [OGBK(5,1,1) model] the nematic phase becomes unstable and only the columnar and the isotropic phases remain.

The present results show that in discotic systems the energetics is in general not cooperative with the entropic factors to enhance nematogenic behavior, but rather leads to a systematic suppression of the nematic phase. We find a similar trend in systems where either stacking or edge-to-edge interactions are dominant. Only for moderate edge-to-edge interactions a weak stabilization of the nematic phase is observed. It can therefore be concluded that the use of particles with dominant homogeneous repulsive or attractive interactions are convenient when tailoring discotic nematogens. The introduction of functional groups with weak directional dispersive interactions at the toroidal rims of the particles may also be beneficial for nematic behavior. However, the incorporation of directional attractive groups demands for a fine balance of the energetic and entropic contributions to the free energy; otherwise the columnar arrangements become favored. In fact, the above argumentation could be reversed if the aim is to promote the columnar phases and extend their robustness for specific applications. To this respect, it is interesting to take into consideration the fact that pair interactions enhancing columnar stability need not be of stacking type. The incorporation of peripheral side groups to the particles that increase the directionality of the interactions has similar effects, and is often chemically more convenient than the modification of the central core of the particles. The fact that enhanced stacking interactions stabilize columnar phases at the expense of nematic phases may be more intuitively rationalized than the observation that enhanced edge-edge interactions have the same effect. It should be realized, however, that in a typical hexatic columnar arrangement stacking interactions for each given particle take place just with the two neighboring particles in the same column. In contrast, edge-edge interactions involve particles from the six adjacent columns [14].

From a more fundamental point of view, the results of the present study rely on the realistic properties of the OGBK model. On one hand, this model introduces explicit orientational interactions, in contrast to the original Kihara fluids for which the same pair interaction is assigned to all particle orientations, provided that the minimum distance between the particles stays constant. On the other hand, the spherocylinder shape is expected to provide a more realistic coarse-grained representation of the overall shape of discotic molecules and colloids than other models employed in the past for discotics. Among these, the ellipsoidal Gay-Berne model is the one most extensively employed in previous studies. For this latter model, the nematic phase dominates the phase diagram over a wide range of potential parameters, even for particles of small anisotropy [19]. This behavior is not consistent with practical experience (nematic phases are not present in discotics of low anisotropy) and is related to the fact that columnar phases are symmetry forbidden in the discotic hard ellipsoidal model [20,21], and enter the Gay-Berne phase diagram from energetic (not steric) driving forces. In contrast, for the OGBK model energetic and steric forces are cooperative for the columnar phases, though not so for the nematic phases.

In turn, the quest for robust, broadly stable discotic nematogens demands strategies alternative to energetics. Possible pathways could probe the introduction of polidispersity in the particles sizes [22,23], the dimerization of discotic units [24], or the incorporation of side chains that contribute to the steric hindrance of stacking [25]. We are currently exploring these alternatives in similar simulation studies with discotic spherocylinder models.

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