Role of stringlike, supramolecular assemblies in reentrant supernematic liquid crystals

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(Received 7 January 2011; published 13 May 2011)

Using a combination of isothermal-isobaric Monte Carlo and microcanonical molecular dynamics we investigate the relation between structure and self-diffusion in various phases of a model liquid crystal using the Gay-Berne-Kihara potential. These molecules are confined to a mesoscopic slit pore with atomically smooth substrate surfaces. As reported recently [see M. G. Mazza et al., Phys. Rev. Lett. 105, 227802 (2010)], a reentrant nematic (RN) phase may form at sufficiently high pressures and densities. This phase is characterized by a high degree of nematic order and a substantially enhanced self-diffusivity in the direction of the director \( \hat{n} \) that exceeds that of the lower-density nematic and an intermittent smectic-A phase by about an order of magnitude. Here we demonstrate that the unique transport behavior in the RN phase may be linked to a confinement-induced packing effect that causes the formation of supramolecular, stringlike conformations. The strings consist of several molecules traveling in the direction of \( \hat{n} \) as individual “trains” consisting of chains of molecular “cars.”

DOI: 10.1103/PhysRevE.83.051704 PACS number(s): 61.30.Hn, 66.10.C-, 64.70.M-, 61.30.Gd

I. INTRODUCTION

The richness of the phase diagram of liquid crystals offers a multitude of interesting problems for both theoretical and experimental studies [1]. Generally, as the temperature \( T \) is lowered (or equivalently as the pressure is increased) a substance undergoes a series of transitions from a high symmetry phase to a low symmetry phase [2]. A high (low) symmetry phase consists of configurations invariant under a large (small) number of symmetry transformations. In the case of liquid crystals, one typically finds at high \( T \) an isotropic phase (I) (high symmetry). Then at lower \( T \) a nematic phase appears in which rotational invariance is broken by selecting a preferential molecular orientation. At even lower \( T \) translational invariance is broken further when a smectic phase appears characterized by the formation of molecular layers. Finally, a crystalline solid forms at rather low \( T \) that is the phase of lowest symmetry in the sequence according to our above definition. The reason for this behavior is quite general: Entropy decreases with \( T \). It may therefore come as a surprise when a phase of higher symmetry appears again in the sequence of phase transitions to states of progressively lower symmetry. This interesting feature is referred to as reentrancy. Reentrant behavior is found in several physical systems. Examples include charged colloids [3], molecular (self-)assemblies [4,5], discotic liquid crystals [6], liquid crystals with a rectangular core [7], the ferroelectric transition of smectic C phases [8], and chiral liquid crystals [9]. Even in quantum gases [10] and in a finite \( T \) quantum field theory [11] reentrant phase transitions have been observed.

In liquid crystals reentrancy was first discovered by Cladis [12] in 1975. A sequence of nematic (N), smectic A (sm-A), and reentrant nematic (RN) was found by cooling a liquid crystal binary mixture. Later a pure compound subject to high pressure and in the supercooled state was found to have a RN phase [13,14]. Then Hardouin et al. [15] first discovered a RN phase in pure liquid crystals at atmospheric pressure. For comprehensive reviews on the subject see Refs. [16] and [17].

The theoretical understanding of the RN phase for polar and nonpolar compounds has mainly focused on concepts of dimerization and frustration and association [18–20]. For example, Berker et al. used a dipolar potential that generates a frustrated state between ferroelectric and antiferroelectric interactions [18,19]. Considering a triplet of these dipoles, the smectic layer can be destabilized when cancellations between competing forces occur. This leads to formation of a RN phase as a translationally disordered state. Ferrarini et al. exploited the processes of association and isomerization to predict the formation of RN phases within a mean-field type of theory [21].

De Miguel et al. [22] used Monte Carlo (MC) simulations of a bulk fluid of hard ellipsoids with square-well attraction to study the sm-A-RN transition in nonpolar compounds to which the dimerization theories do not apply. However, these authors [22] consider a fluid of parallel molecules with no rotational degrees of freedom, which makes the model somewhat artificial.

The dynamics of a RN system is notably less well understood. Although the general belief is that N and RN phases do not differ dramatically in their dynamics, there is some experimental indication suggesting the contrary. For example, distinct differences in the molecular dynamics in the N and RN phases can be concluded from corresponding changes in the nuclear magnetic resonance (NMR) relaxation times reported in Refs. [23–26]. Moreover, measurements in the vicinity of the sm-A-RN phase transition show a marked increase in the ratio of electrical conductivities along the optic axis and perpendicular to it [27] (see also Sec. IIf from Ref. [17]). A more detailed account of the present experimental state of the art is postponed until Sec. IV.

Recently we [28] studied self-diffusion in the RN phase for a system of rodlike mesogens where the interaction between a pair of rods takes into account both a realistic shape of the molecules and the orientation dependence of their interaction. Unlike de Miguel et al. [22] we allowed our molecules to...
rotate as freely as the specific thermodynamic conditions permit. We could then demonstrate \cite{28} that, on account of the high degree of nematic order, diffusion in the direction of the nematic director may be enhanced by about an order of magnitude over that characteristic of lower-density N or sm-A phases. The combination of a high degree of nematic order with a substantially enhanced self-diffusivity in the direction of the nematic director prompted us to refer to liquid crystals in the RN phase as “supernematics” \cite{28}. Enhanced self-diffusivity in the RN phase bears a striking similarity to “levitation” in zeolites. Experiments have demonstrated the self-diffusion coefficient to pass through a maximum when the size of a diffusant molecule is comparable to the pore size; that is, enhanced diffusivity is observed as a result of severe confinement to tiny voids in the host material (see, for example, Ref. [29]).

We could explain this unusually enhanced self-diffusion quantitatively in terms of a severely reduced rotational configurational entropy \cite{28}. However, the relation between self-diffusion and structural features of the RN phase has not yet been explored. In fact, as we shall show in this work the RN phase is characterized by unique conformations of entire groups of its molecules to which we refer as “strings.” Strings may be thought of as trainlike arrangements of several molecules that stay together as molecular “cars” and diffuse as a supramolecular entity. As we argue below it is the fairly high pressure that keeps the trains together and that allows them to overcome the attractive interactions between molecules pertaining to neighboring trains.

Finally, we note that an improved understanding of the dynamics of liquid crystals is not only of academic interest but may also be important from a purely practical point of view. For example, by pumping liquid crystalline material through vesicles, that may be perceived as confined geometries, spiders can spin silk with exceptional materials properties that result essentially from the transport of liquid crystalline proteins. Materials with properties comparable to spider silk cannot be produced in the laboratory to date (see Fig. 2 in Ref. [30]).

\begin{equation}
\mathbf{H} = \sum_{i=1}^{N} \frac{P_i^2}{2m} + \sum_{i=1}^{N} \sum_{a=x,y} \frac{L_{i\alpha}^2}{I} + U(\mathbf{R}, \mathbf{\Gamma}),
\end{equation}

where $P \equiv (p_1, p_2, \ldots, p_N)$ are the linear momenta conjugate to the set of center-of-mass positions $\mathbf{R} \equiv (r_1, r_2, \ldots, r_N)$ and $\mathbf{\Gamma} \equiv (\gamma_1, \gamma_2, \ldots, \gamma_N)$ are the Euler angles specifying the orientation of each molecule. For the special case of spherocylinders with two rotational degrees of freedom, $\gamma_i = (\theta_i, \phi_i)$ is a two-dimensional vector composed of two of the three Euler angles. In Eq. (1), $L_{i\alpha}$ is the component of the angular momentum referred to the body-fixed principal axis $\alpha$ of molecule $i$, $m$ is the molecular mass, and

\begin{equation}
I = \frac{3m}{3L + R} \left( \frac{8R^3}{15} + \frac{3R^2L}{4} + \frac{RL^2}{3} + \frac{L^3}{12} \right)
\end{equation}

is the moment of inertia of a spherocylinder.
In a computer simulation [both MC and molecular dynamics (MD)] the key quantity is the configurational potential energy $U(R, \vec{U})$ of the system [see, for example, Eqs. (A2), (A5b), or (A7)] where $\vec{U} \equiv \vec{u}_1, \vec{u}_2, \ldots, \vec{u}_N$ is a set of unit vectors specifying the orientation of the molecules in a three-dimensional space-fixed Cartesian coordinate system (see Fig. 1). Elements of the set $\vec{U}$ are related to corresponding elements of the set $\Gamma$ via

$$d\vec{u}_i = \sin \theta_i d\theta_i d\phi_i, \quad i = 1, \ldots, N$$  \hspace{1cm} (3)

In the general case of a confined fluid $U(R, \vec{U})$ can be decomposed into a fluid-fluid (ff) and a fluid-substrate (fs) contribution. Assuming pairwise additive interactions the former can be cast as

$$U_{ff}(R, \vec{U}) = \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} u_{ff}(d_{ij}^{m})$$  \hspace{1cm} (4)

whereas the latter may be expressed as

$$U_{fs}(R, \vec{U}) = \sum_{k=1}^{2} \sum_{i=1}^{N} u_{fs}(d_{ik}^{m})$$  \hspace{1cm} (5)

In Eqs. (4) and (5), $u_{ff}$ and $u_{fs}$ represent the specific model potential adopted to describe the intermolecular interaction between two rodlike molecules and between a rodlike molecule and a planar, structureless solid substrate, respectively. In this work we adopt the so-called Gay-Berne-Kihara (GBK) model [31]. In the GBK model the interaction between a pair of spherocylinders depends on the relative molecular orientation through the function $d_{ij}^{m}(r_{ij}, \hat{u}_i, \hat{u}_j)$, which depends on the center-of-mass distance vector $r_{ij} \equiv r_i - r_j$ and the orientations of molecules $i$ and $j$ such that $d_{ij}^{m}$ is actually the minimum distance between that pair of molecules. More specifically,

$$u_{ff} = 4\epsilon_{ff}(|\hat{\vec{r}}_{ij}|, \hat{\vec{u}}_i, \hat{\vec{u}}_j) \left[ \left( \frac{a}{d_{ij}^{m}} \right)^{12} - \left( \frac{a}{d_{ij}^{m}} \right)^{6} \right],$$  \hspace{1cm} (6)

where $\hat{\vec{r}} \equiv r/r$ and $r \equiv |r|$. In Eq. (6) the function

$$\epsilon_{ff}(\hat{r}_{ij}, \hat{u}_i, \hat{u}_j) = \epsilon_{ff} \left\{ 1 - \chi \left[ \left( \hat{\vec{r}}_{ij} \cdot \hat{\vec{u}}_i + \hat{\vec{r}}_{ij} \cdot \hat{\vec{u}}_j \right)^2 \right] + \left( \hat{\vec{r}}_{ij} \cdot \hat{\vec{u}}_i - \hat{\vec{r}}_{ij} \cdot \hat{\vec{u}}_j \right)^2 \right\} \frac{1}{1 - \chi^2 (\hat{\vec{u}}_i \cdot \hat{\vec{u}}_j)^2}$$  \hspace{1cm} (7)

describes the orientation dependence of the interaction strength where the parameters $\chi$ and $\chi'$ are given by

$$\chi = \frac{k^2 - 1}{k^2 + 1},$$  \hspace{1cm} (8a)

$$\chi' = \frac{\sqrt{k'} - 1}{\sqrt{k'} + 1}.$$  \hspace{1cm} (8b)

In these last two expressions parameters $k = L + 1$ (in units of $a$), and $k'$ may be thought of as the interaction strength for a side-side relative to an end-end configuration of a pair of spherocylinders. Figure 2 shows the strong dependence of $u_{ff}$ on molecular orientation so that a side-side configuration of a molecular pair is the energetically most favored one. One also notices from Fig. 2 that both the location of the potential minimum as well as the range of distances over which $u_{ff}$ becomes repulsive depend very little on the intermolecular orientation as one would expect on account of the spherocylindrical shape of the molecules.

Similarly $d_{fs}^{m}(z_{ik}, \hat{u}_i)$ introduced in Eq. (5) is the minimum distance between a spherocylinder with orientation $\hat{u}_i$ whose center of mass is at a vertical distance $z_{ik} = z_i \pm s_i/2$ from the lower ($k = 1$) and upper ($k = 2$) substrate located at $-s_i/2$ and $+s_i/2$ along the $z$ axis of a space-fixed Cartesian coordinate system, respectively. The role of confining walls is to introduce an external field that facilitates the formation of ordered phases at lower pressures. If set up favorably a substrate can orient molecules in its vicinity even though the entire confined liquid crystal is still in the I phase. Thereby, confinement assists the formation of more ordered phases. Assuming the substrates to be planar, $d_{fs}^{m}$ can easily be determined as the smallest of the two distances of both end points of a spherocylinder from the substrate plane. The corresponding function $d_{fs}^{m}(r_{ij}, \hat{u}_i, \hat{u}_j)$ is more complex but can be computed numerically using an efficient algorithm proposed by Vega and Lago [32]. Following Ref. [28] we model the fluid-substrate interaction via

$$u_{fs} = 4\epsilon_{fs}\rho_s \left[ \left( \frac{a}{d_{ik}^{m}} \right)^{10} - \left( \frac{a}{d_{ik}^{m}} \right)^{4} \right] g(\hat{u}_i),$$  \hspace{1cm} (9)

where the parameter $\epsilon_{fs}$ controls the strength of interaction similar to $\epsilon_{ff}$ in Eq. (7) and $\rho_s \sigma^2 = 2^{-1/3}$ is the areal density of a single layer of atoms arranged according to the (100) plane of the face-centered cubic lattice. The diameter $\sigma$ of these substrate atoms is taken to be the same as the diameter of a spherocylinder of the confined fluid phase. To obtain Eq. (9) we assume the interaction between the point on the spherocylinder closest to the nearest substrate atom to be described by a conventional Lennard-Jones potential. Holding both the center-of-mass position $r_i$ and the orientation $\vec{u}_i$ fixed, one then averages the interaction with the substrate atom over the entire substrate area. Notice that this procedure gives rise to a prefactor $\frac{1}{2}$ in front of the repulsive term in Eq. (9), which we have deliberately omitted for convenience.

In Eq. (9), $0 \leq g(\hat{u}) \leq 1$ is the so-called anchoring function. It permits to discriminate energetically different orientations of a molecule with respect to the substrate plane. In this paper we employ

$$g(\hat{u}) = \left( \hat{u} \cdot \hat{e}_x \right)^2 + \left( \hat{u} \cdot \hat{e}_y \right)^2,$$  \hspace{1cm} (10)

where $\hat{e}_x$ is a unit vector pointing along the $\alpha$ axis of a space-fixed Cartesian coordinate system. Hence, any molecular arrangement parallel with the substrate plane is energetically favored, whereas a homotropic alignment of a molecule ($\hat{u} \parallel \hat{e}_z$) receives an energy penalty by “switching off” the fluid-substrate attraction altogether.

At this stage a couple of additional comments apply. For example, the reader may notice that Eqs. (7) and (8) are identical to the corresponding expressions in the well-known Gay-Berne (GB) model of liquid crystals [33]. However, in the GB model a liquid crystal molecule is perceived as an ellipsoid of revolution. This is effected by replacing the
The relative orientation. This is achieved by setting
molecules depends only on the minimum distance but not on
spherocylinder, but the interaction strength between a pair of
molecules to be located in the
molecular shape. In generating the plots we assumed a pair of
plane with a perfectly parallel
orientation (i.e., \( \hat{u}_i \cdot \hat{u}_j = 1 \)) as a special case (see also Fig. 1). Both
x and y are given in units of \( \sigma \). Note that the GBK model combines
the molecular shape of the K model with the interaction anisotropy
of the GB model.

function \( d_{ij}^{\parallel}(\mathbf{r}_{ij}, \hat{u}_i, \hat{u}_j) \) in Eq. (6) by one that accounts properly
for the shape of a molecule in the GB model [see, for example,
Eq. (4) of Ref. [34]]. The GBK model is also closely related
to the so-called Kihara (K) model [35] of a liquid crystal
[36]. In this latter model a molecule is again perceived as a
spherocylinder, but the interaction strength between a pair of
molecules depends only on the minimum distance but not on
the relative orientation. This is achieved by setting \( \kappa' = 1 \) in
Eq. (8b) such that \( \varepsilon_{ij}(\mathbf{r}_{ij}, \hat{u}_i, \hat{u}_j) = \varepsilon_{ij} \) in Eq. (7). The shapes of
molecules in the K, GB, and GBK models resulting from these
manipulations are illustrated by the contour plots in Fig. 3.

B. Numerical details

The simulations (both MC and MD) performed are based
on systems containing \( N = 1500 \) molecules. Quantities of
interest will be expressed in customary dimensionless (i.e.,
“reduced”) units. For example, length will be expressed in units of \( \sigma \), energy in units of \( \varepsilon_{ij} \), temperature in units of \( \varepsilon_{ij} / k_B \), time in units of \( (\sigma^2 m / \varepsilon_{ij})^{1/2} \) using \( m = 1 \), and pressure \( P_{ij} \) in units
of \( k_B T / \sigma^3 \) where \( P_{ij} = \frac{1}{2}(P_{xx} + P_{yy}) \) is related to diagonal
components of the pressure tensor \( \mathbf{P} \) acting in the \( x\text{-}y \) plane.

We employ MC simulations in an isothermal-isobaric
ensemble where we use \( N, T, P_{ij} \), and \( s_N \) as input parameters.
In all the simulations we fix \( s_N = 19 \) and consider \( T = 4.0 \) and
6.0. To reduce the computational cost interactions between
fluid molecules are cut off beyond a minimum distance \( d_{ij}^\parallel = 3 \). In addition, we employ a conventional Verlet neighbor list
where molecules up to a minimum distance of 8 are included
as neighbors [37]. In the \( x \) and \( y \) directions periodic boundary
conditions are applied.

In MC we employ the algorithm of Schoen [38] with one
important modification. Rather than changing the area \( A \) of
the simulation box in the sense of a similarity transformation
we allow the individual side lengths \( s_{ij} (\alpha = x, y) \) to vary
independently such that the shape of the simulation cell may
change during the course of a simulation. This is important to
preserve the in-plane isotropy of \( \mathbf{P} \) especially in highly ordered
N, sm-A, or RN phases. Our runs start from a sufficiently low
pressure in the I phase. In the initial configuration molecules
are perfectly aligned and then allowed to relax to the I state.
The last configuration of this run is then used as a starting con-
figuration of the next run at a slightly higher \( P_I \). We continue
with such a compression sequence until the last state point of
the highest pressure of interest has been reached. We refer to
a MC step as \( N \) attempted displacements or rotations and one
attempted change of \( s_{ij} \). Displacements and rotations as well
as changes of \( s_{ij} \) for \( \alpha = x \) or \( \alpha = y \) are performed with equal
probability. Our runs are based upon \( 3 \times 10^5 \) equilibration
steps followed by \( 2 \times 10^5 \) production steps for thermodynamic
states sufficiently far away from any phase transition; around
these transitions the number of production steps was enlarged
to \( 7 \times 10^5 \). However, in changing \( A \) as described care has to be
taken that none of the instantaneous side lengths \( s_{ij} \) becomes
shorter than twice the neighbor-list cutoff given above.

MC simulations are mainly employed to generate suitable
starting configurations for the subsequent MD simulations. In
addition, MC is used to independently verify the correctness
of the MD simulations through a comparison of equilibrium
properties accessible to both types of simulations. In MD we
employ the velocity Verlet algorithm for linear molecules in
the implementation suggested by Ilnytskyi and Wilson [39].
The iterative solution of the equations of motion is initiated
by using the last configuration of the MC simulation at the
same state point as a starting configuration where velocities
are taken at random from a Maxwell-Boltzmann distribution at
the desired temperature. This starting configuration is
equilibrated for another \( 10^6 \) time steps of \( \delta t = 0.02 \) using a
simple velocity rescaling thermostat. The equilibrated system
is then monitored for another \( 2 \times 10^7 \) time steps with no
applied thermostat. During this part of the run the integration
time step is reduced to \( \delta t = 10^{-4} \).

III. RESULTS

A. Structure of ordered liquid-crystalline phases

To characterize the structure of N, sm-A, and RN phases
we begin by introducing suitably defined order parameters.
For nematic phases this is accomplished via the so-called
alignment tensor defined as [40]

\[
\mathbf{Q} = \frac{1}{2N} \sum_{i=1}^{N} (3\mathbf{u}_i \otimes \mathbf{u}_i - \mathbf{1}),
\]

FIG. 3. (Color online) Plots of the equipotential contour plot
\( u_q / \varepsilon_q \) for the GBK (bottom), K (top left), and GB (top right) models
(see text); color code shown alongside. The area in white is defined
through the inequality \( u_q > 0 \), therefore approximately representing
the molecular shape. In generating the plots we assumed a pair of
molecules to be located in the \( x\text{-}y \) plane with a perfectly parallel
orientation (i.e., \( \hat{u}_i \cdot \hat{u}_j = 1 \)) as a special case (see also Fig. 1). Both
x and y are given in units of \( \sigma \). Note that the GBK model combines
the molecular shape of the K model with the interaction anisotropy
of the GB model.
where “\(\otimes\)” denotes the direct (i.e., dyadic) product and \(I\) is the unit tensor. Hence, \(Q\) is a real, symmetric, and traceless second-rank tensor that can be represented by a \(3 \times 3\) matrix. For a given configuration \((\mathbf{R}, \hat{U})\), \(Q\) can be diagonalized in the basis of its three eigenvectors \(\hat{n}_-, \hat{n}_0,\) and \(\hat{n}_+\), with associated eigenvalues \(\lambda_-, \lambda_0,\) and \(\lambda_+\). Conventionally [41], one then defines the Maier-Saupe [42, 43] nematic order parameter \(S = \langle \lambda_+ \rangle\) where angular brackets denote an ensemble (MC) or time average (MD). On account of its definition, \(S = 0\) in the I phase if the orientation of the molecules is perfectly random, whereas \(S = 1\) if the molecules are perfectly aligned with the director \(\hat{n} = \hat{n}_+\) in the nematic phase.

Even though the N phase is characterized by a substantial degree of orientational order the distribution of center-of-mass positions exhibits the typical short-range order characteristic of ordinary fluids where the typical correlation lengths are comparable to the range of intermolecular interactions. This changes in the sm-A phase where molecules do not only align with \(\hat{n}\) but also develop long-range positional order, that is, they form individual layers in the direction of \(\hat{n}\). However, positional order remains short range in directions orthogonal to \(\hat{n}\) such that within a given layer the structure remains fluidlike. Because of the layering of the fluid in the direction of \(\hat{n}\) a suitable quantitative measure of smectic order is given by the leading coefficient of the Fourier transform of the local density \(\rho(r \cdot \hat{n})\)

\[
\Lambda = \frac{1}{N} \left\langle \sum_{i=1}^{N} \exp \left[ \frac{2\pi i (r_i \cdot \hat{n})}{d} \right] \right\rangle,
\]

where \(d\) is the spacing between adjacent sm-A layers. If these layers were ideal, \(d = \kappa\) (see Sec. II A). However, in practice \(d \gtrsim \kappa\) on account of thermal fluctuations. Hence, in each configuration \((\mathbf{R}, \hat{U})\), \(d\) is adjusted such as to maximize \(\Lambda\). From Eq. (12) it is also apparent that \(\Lambda \in [0, 1]\). In the N phase the superposition of the complex exponential functions in Eq. (12) causes \(\Lambda \approx 0\) because in the direction of \(\hat{n}\) a periodic structural feature of periodicity \(d\) does not exist; by a similar token \(\Lambda \approx 1\) in the sm-A phase.

Plots of both \(S\) and \(\Lambda\) are presented in Fig. 4 for \(T = 4.0\) and 6.0. As one can see from the plots, both \(S\) and \(\Lambda\) are small at low pressures indicating the presence of the I phase. Ideally, \(S = 0\) in the I phase but in practice attains small positive values of about 0.2. This is partly due to the substrates which induce a certain degree of nematic order in those portions of the confined liquid crystal that are closest to either substrate. However, a nonvanishing value of \(S\) in the I phase is also due to a small but significant finite-size effect that is well known and has been studied quantitatively in the literature [41, 44]. Here we adopt a value \(S \approx 0.4\) as a sensible heuristic definition of the threshold above which the N phase exists in agreement with the mean-field theory of Maier and Saupe [42, 43]. From Fig. 4 it therefore appears that the N phase forms somewhere above \(P_1 \approx 1.0\) (\(T = 4.0\)) and 1.2 (\(T = 6.0\)), respectively.

Focusing on the lower \(T\) first, \(S\) increases in the N phase with pressure up to \(P_1 \approx 1.7\) indicating the increase of nematic order. Over the same pressure range there are no smectic layers because \(\Lambda \lesssim 0.2\) remains relatively small. However, at \(P_1 \approx 1.8\), smectic layers are forming as reflected by \(\Lambda \gtrsim 0.8\). Simultaneously, \(S\) keeps increasing as well because in the sm-A phase molecules align themselves even better with \(\hat{n}\). The sm-A phase remains stable until \(P_1 \approx 2.2\) has been attained. Beyond this pressure \(S\) remains nearly constant at a high value of about 1.0 whereas \(\Lambda\) drops rapidly until a residual small value of about \(\Lambda \approx 0.1\) is assumed, which remains constant at all higher pressures considered. The drop in \(\Lambda\) with \(P_1\) clearly reflects the disappearance of smectic layers present at lower \(P_1\). Because \(S \approx 1.0\) over the same pressure range, we conclude that at sufficiently high pressures the structure of the confined fluid becomes nematic again in a reentrant fashion. To distinguish the high-pressure from the low-pressure nematic we refer to the former as RN because N and RN phases are separated by an intermittent sm-A phase. At \(T = 6.0\) these general features of the order-parameter plots in Fig. 4 prevail except that \(\Lambda\) never rises above the residual value of about 0.1. Hence, the sm-A phase does not form at this \(T\). Nevertheless, we notice a small, steplike increase at \(P_1 \approx 2.2\) in the plot of \(\Lambda\). At this and all larger pressures considered the nematic order is high and increases even further reflected by a monotonic increase of \(S\) toward its limiting value 1.0. For \(P_1 \gtrsim 2.2\) the confined fluid exhibits structural features of the RN phase (see below). We shall therefore keep the acronym despite the missing intermittent sm-A phase.

To get a better feel for the structure of the confined fluid in the N, sm-A, and RN phases we present configuration “snapshots” from our simulations in Fig. 5. The plot in Fig. 5(a) illustrates the structure of the N phase; One clearly recognizes a preferred net orientation of the molecules but no significant positional order of the center-of-mass distribution. In Fig. 5(b) the layer structure characteristic of the sm-A phase is visible. These layers disappear in the RN phase as shown in Fig. 5(c). However, a large degree of orientational order is preserved
an interval of width
number of molecules with their centers of mass located within
(RN) (see Fig. 4). Areas in dark on top and bottom represent the solid
substances at
always start from an I state point as explained in Sec. II B.
of molecules with the
as one realizes from this latter plot. The apparent alignment
of molecules with the x axis is accidental, because the runs
always start from an I state point as explained in Sec. II B.
A more quantitative analysis of the structure of confined
liquid crystals in the various ordered phases is enabled by
plots of the local density
\[ \rho(z) = \left( \sum_{i=1}^{N} \delta(z - z_i) \right) = \frac{1}{\delta_z} \frac{N(z)}{A}, \]
where \( \delta(z - z_i) \) denotes the Dirac \( \delta \) function, \( N(z) \) is the
number of molecules with their centers of mass located within
a interval of width \( \delta_z = 0.1 \), and \( A = s_x s_y \) is the instantaneous
area of the simulation cell of side length \( s_x (\alpha = x, y) \) in the
\( \alpha \) direction. Hence, \( \rho(z) \) is a measure of the probability of
finding the center of mass at a specific position \( z \). Plots in
Fig. 6 illustrate the local structure of the confined liquid crystal
in the direction of the substrate normal (i.e., perpendicular to the
director \( \hat{n} \)). As is well known from simple fluids [45],
in confinement \( \rho(z) \) is an oscillatory function of position
sufficiently close to the substrate surfaces. The oscillations
indicate that molecules arrange their centers of mass in
individual layers parallel with the substrate. The location of a
molecular layer is therefore indicated by a peak in \( \rho(z) \). In the
immediate vicinity of the solid substrate \( \rho(z) \to 0 \) because of the
diverging fluid-substrate repulsion as \( |z| \to s_z/2 \).

These general features may be seen from the plots in
Fig. 6. One notices that in the N phase oscillations in \( \rho(z) \)
are restricted to the immediate vicinity of the solid substrates
[see Fig. 6(a)]. The oscillations decay exponentially as \( |z| \to 0 \)
with a correlation length determined by bulk properties [46],
whereas the spacing between neighboring layers reflects the
molecular shape [47]. In the N phase a bulklike region of
considerable width exists in which \( \rho(z) \) is constant as the plot in
Fig. 6(a) reveals. On the contrary, layering is much more
pronounced in the sm-A phase as a comparison of plots in
Figs. 6(a) and 6(b) indicates: Peaks in Fig. 6(b) are taller,
and because a bulk-like region is absent the entire confined
fluid is organized in layers. However, the layered structure
becomes weaker as one approaches the center of the slit pore,
as reflected by the decay of \( \rho(z) \) in Fig. 6(b). Finally, in the
RN phase layering is even more pronounced, as the plot in
Fig. 6(c) shows. Moreover, plots in Fig. 6(b) and 6(c) reveal
another subtle structural change. Counting maxima in the plots
of \( \rho(z) \) one realizes that one additional layer of molecules is
present in the RN compared with the sm-A phase. The presence
of this additional layer points to a more efficient packing of
molecules as far as the arrangement of their centers of mass is
concerned. A more efficient packing becomes possible because the
layered structure characteristic of the sm-A phase [see Fig. 5(b)]
is lost in the RN phase [see Fig. 5(c)].

Next, at \( T = 6 \) one realizes from Fig. 7 a similar formation of
an additional molecular layer but without occurrence of
an intermittent sm-A phase. Plots in Figs. 7(a) show that for
two state points in the N phase an increase in pressure only
causes the layers already present to become more distinct.
For example, \( \rho(z) \) drops to zero in regions between individual
layers at the higher pressure, whereas \( \rho(z) \) remains nonzero
over the corresponding ranges at the lower pressure. The plot
in Fig. 7(b) corresponds to a state point where the confined
fluid undergoes the subtle reorganization that will eventually
lead to the growth of an additional layer. As one approaches
the midplane located at \( z = 0 \) individual peaks in \( \rho(z) \) first
broaden and eventually split up into two unresolved peaks. At
an even higher pressure considered in Fig. 7(c) we realize that

![Fig. 5. (Color online) “Snapshots” of characteristic configurations at \( T = 4.0 \); (a) \( P_1 = 1.6 \) (N), (b) \( P_1 = 2.1 \) (sm-A), (c) \( P_1 = 2.9 \) (RN) (see Fig. 4). Areas in dark on top and bottom represent the solid substrates.](image1)

![Fig. 6. (Color online) Local density \( \rho(z) \) as a function of \( z \) for \( T = 4.0 \); (a) \( P_1 = 1.7 \) (N), (b) \( P_1 = 2.2 \) (sm-A), (c) \( P_1 = 2.3 \) (RN).](image2)
the fluid has completed its structural reorganization and a new fluid layer emerges, as we can see by comparing this plot with the fluid has completed its structural reorganization and a new fluid layer emerges, as we can see by comparing this plot with

In our terminology a “string” is a sequence of molecules arranged in space like individual cars of a train with their long axes all pointing in the same direction. The “snapshot” of a typical configuration presented in Fig. 5(c) already indicates that in the RN phase molecules appear in stringlike arrangements. In mathematical terms an ideal string can therefore be defined through the relations

where, of course, one of the two scalar products in Eq. (14b) is redundant. In practice, however, small deviations from perfect alignment of molecules in a string arise on account of thermal fluctuations. A good measure of the extent to which a pair of molecules is arranged in a stringlike conformation approximately may be defined by decomposing the distance vector \( \mathbf{r}_{ij} \) between the centers of mass of nearest-neighbor molecules \( i \) and \( j \) into components parallel and perpendicular to \( \mathbf{u}_i \) through the expressions (see Fig. 1)

For a stringlike configuration of a pair of molecules one anticipates \( r^\perp_{ij} \rightarrow 0 \). However, a second typical conformation characterized by relatively small values of \( r^\perp_{ij} \) is conceivable. In this conformation molecules are arranged in a shifted side-side arrangement [see Fig. 8(a)]. Plots of configurational snapshots in Fig. 5 clearly show that also unshifted side-side arrangements exist both in the N and in the RN phase. This is because they are energetically favored according to Fig. 3(a). However, they are also present to some extent in other phases as snapshots in Figs. 5(a) and 5(c) indicate. To eliminate these unwanted unshifted side-side conformations in favor of only shifted ones it is prudent from an operational point of view to consider only the subset \( \{ \tilde{\mathbf{r}}_{ij}^\perp \} \) defined through

where we arbitrarily take \( \delta_c = 0.2 \) and \( \delta_{\cos \theta} = 0.98 \). To see that this rather complex definition selects only those conformations sketched in Figs. 8(a) and 8(b) one needs to realize that the first of the three conditions in Eq. (16) selects nearest neighbors \( \{ j \} \) of a given molecule \( i \), the second condition favors head-tail-like conformations, whereas the third one selects molecules with nearly perfectly aligned long molecular axes. It is then convenient to introduce the probability

for a quantitative discussion of the formation of stringlike structures where \( P_0 \) is a normalization constant that we determine via

FIG. 7. As Fig. 6, but for \( T = 6.0 \): (a) \( P_0 = 2.3 \) (—) and 2.4 (--), (b) \( P_0 = 2.5 \), (c) \( P_0 = 2.6 \). Note that all parts of the figure refer to RN states. Inset is a magnification of curves for \( P_0 = 2.4, 2.5, \) and 2.6 around \( z = 0 \).

FIG. 8. (Color online) Sketch of a pair of spherocylinders (see Fig. 1). (a) Shifted side-side conformation, (b) As (a), but for a stringlike conformation. The wedge-shaped areas corresponds to the solid angle \( \int_0^{\pi/2} d\theta \mathcal{P}(r^\perp) \equiv 1 \).
phase at \( r^\perp < 0.5 \) corresponds to stringlike conformations schematically illustrated by the plot in Fig. 8(b). Were the stringlike conformation perfect one would anticipate a peak of \( \mathcal{P}(r^\perp) \) at \( r^\perp = 0 \). However, on account of thermal fluctuations these ideal stringlike conformations are only infrequently observed. For example, closer scrutiny would reveal that \( \mathcal{P}(r^\perp) \neq 0 \) at \( r^\perp = 0 \) indicating that a very small fraction of molecules does, in fact, assume an ideal stringlike conformation. As \( P_1 \) increases one notices that both peaks of \( \mathcal{P}(r^\perp) \) shift to progressively smaller \( r^\perp \). This fact reflects an arrangement of molecules in more perfect stringlike conformations with increasing pressure as one would expect intuitively.

One also notices from plots in Figs. 9(a) and 9(b) that the curves seem to intersect at isolated points corresponding to characteristic values of \( r^\perp \). These intersections may be interpreted as “isosbestic” points (derived from the Greek words \textit{isos}: equal, the same, and \textit{sbestos}: extinguishable) \( [48] \), a concept widely known in spectroscopy. The occurrence of isosbestic points is relatively simple to grasp. We assume that \( \mathcal{P}(r^\perp) \) can be decomposed into a sum of three contributions:

1. A probability distribution centered at \( r^\perp \approx 1.0 \) corresponding to a population of shifted side-side molecular conformations [see Fig. 8(a)].
2. A probability distribution centered at \( r^\perp \approx 0.25 \) corresponding to a population of shifted stringlike molecular conformations [see Fig. 8(b)], and
3. A probability distribution representing all other molecular conformations satisfying Eq. (16) and embracing the entire range of \( r^\perp \).

For sufficiently large \( P_1 \) the distributions of 1 and 2 can be assumed to be well separated, whereas 3 may be thought of as a broad background distribution. Intersections between distributions 1 and 3 or between 2 and 3, respectively, will give rise to isosbestic points. As \( P_1 \) increases, distributions 1 and 2 become sharper and increase in height at the expense of the background distribution 3. Moreover, maxima of both distributions 1 and 2 shift to lower values of \( r^\perp \), indicating an increase in order. Importantly, the emergence of two well-defined peaks in \( \mathcal{P}(r^\perp) \) is a fingerprint of the RN phase and could therefore be taken as computational evidence to detect RN phases even though its experimental significance may be limited. Incidentally, at low \( P_1 \) (i.e., in the I, N, or sm-A phase) the only important distributions are 1 and 2 because stringlike conformations are statistically irrelevant. Consequently, only one isosbestic point exists as shown in the insets of Fig. 9.

![FIG. 9. (Color online) Probability distribution \( \mathcal{P}(r^\perp) \) (see Figs. 1 and 8, Eqs. (15)–(17)). (a) \( T = 4.0 \) and \( P_2 = 23.2 (\checkmark) \), \( P_3 = 2.6 (\square) \), and \( P_3 = 1.3 (\checkmark) \), all in the RN phase; inset: \( P_3 = 0.9 (\checkmark) \) (I), \( P_3 = 1.4 (\times) \) (N), and \( P_3 = 1.2 (\square) \) (sm-A). (b) \( T = 6.0 \) and \( P_3 = 2.2 (\checkmark) \), \( P_3 = 2.4 (\triangle) \), \( P_3 = 2.5 (\square) \), and \( P_3 = 2.9 (\times) \), all in the RN phase; inset: \( P_3 = 1.1 (\checkmark) \) (I) and \( P_3 = 1.7 (\times) \) (N).](image)

In the actual simulations we obtain \( \mathcal{P}(r^\perp) \) as a histogram using \( \delta r^\perp = 0.02 \) as the bin width.

Plots in Fig. 9 show \( \mathcal{P}(r^\perp) \) for different temperatures and pressures in the I, N, sm-A, and RN phases. At sufficiently low pressures it is evident from the insets in Figs. 9(a) and 9(b) that \( \mathcal{P}(r^\perp) \) increases monotonically with \( r^\perp \) and reaches a broad maximum located approximately at \( r^\perp \approx 1.25 \) irrespective of whether the I, N, or sm-A phase is considered. That \( \mathcal{P}(r^\perp) \) rises with \( r^\perp \) may be ascribed to molecules in the I, N, and sm-A phase that arrange their long axes locally parallel to a certain degree. This is solely caused by the intermolecular interaction potential which favors local side-side conformations of molecules.

In the RN phase the form of \( \mathcal{P}(r^\perp) \) is completely different. Here the plots in Fig. 9(a) and 9(b) exhibit two maxima. The largest one slightly above \( r^\perp \approx 1.0 \) corresponds to conformations in which neighboring particles are arranged in the shifted side-side conformation depicted schematically in Fig. 8(a). Note that these values of \( r^\perp \) are slightly below the position of the minimum of the interaction potential (see Fig. 2). The secondary maximum of \( \mathcal{P}(r^\perp) \) in the RN phase at \( r^\perp < 0.5 \) corresponds to stringlike conformations schematically illustrated by the plot in Fig. 8(b). Were the stringlike conformation perfect one would anticipate a peak of \( \mathcal{P}(r^\perp) \) at \( r^\perp = 0 \). However, on account of thermal fluctuations these ideal stringlike conformations are only infrequently observed. For example, closer scrutiny would reveal that \( \mathcal{P}(r^\perp) \neq 0 \) at \( r^\perp = 0 \) indicating that a very small fraction of molecules does, in fact, assume an ideal stringlike conformation. As \( P_1 \) increases one notices that both peaks of \( \mathcal{P}(r^\perp) \) shift to progressively smaller \( r^\perp \). This fact reflects an arrangement of molecules in more perfect stringlike conformations with increasing pressure as one would expect intuitively.

One also notices from plots in Figs. 9(a) and 9(b) that the curves seem to intersect at isolated points corresponding to characteristic values of \( r^\perp \). These intersections may be interpreted as “isosbestic” points (derived from the Greek words \textit{isos}: equal, the same, and \textit{sbestos}: extinguishable) \( [48] \), a concept widely known in spectroscopy. The occurrence of isosbestic points is relatively simple to grasp. We assume that \( \mathcal{P}(r^\perp) \) can be decomposed into a sum of three contributions:

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3. A probability distribution representing all other molecular conformations satisfying Eq. (16) and embracing the entire range of \( r^\perp \).

For sufficiently large \( P_1 \) the distributions of 1 and 2 can be assumed to be well separated, whereas 3 may be thought of as a broad background distribution. Intersections between distributions 1 and 3 or between 2 and 3, respectively, will give rise to isosbestic points. As \( P_1 \) increases, distributions 1 and 2 become sharper and increase in height at the expense of the background distribution 3. Moreover, maxima of both distributions 1 and 2 shift to lower values of \( r^\perp \), indicating an increase in order. Importantly, the emergence of two well-defined peaks in \( \mathcal{P}(r^\perp) \) is a fingerprint of the RN phase and could therefore be taken as computational evidence to detect RN phases even though its experimental significance may be limited. Incidentally, at low \( P_1 \) (i.e., in the I, N, or sm-A phase) the only important distributions are 1 and 2 because stringlike conformations are statistically irrelevant. Consequently, only one isosbestic point exists as shown in the insets of Fig. 9.

### B. Self-diffusivity in liquid crystalline phases

The formation of stringlike conformations has important ramifications as far as dynamic properties of the RN phase are concerned. To illustrate this we begin by considering a persistence probability

\[
\sigma(\tau) \equiv \left\langle \frac{\sum_{i,j} P_2[n_{ij}(t + \tau)]}{\sum_{i,j} P_2[n_{ij}(t)]} \right\rangle,
\]

(19)
defined as the correlation function of the angle between a pair of molecules \((i, j)\) which at the initial time \(t\) satisfy the conditions for a stringlike conformation introduced in Eq. (16), and where \(P_2(x) \equiv \frac{1}{2}(3x^2 - 1)\) is the second Legendre polynomial. Subscript “\(R\)” is attached to the angular brackets to emphasize that averaging involves a sufficiently large number of statistically uncorrelated time origins, which implicitly invokes the principle of stationarity of temporal correlation functions in equilibrium systems [49]. In Eq. (19), \(\eta_{ij} \equiv \hat{u}_i \cdot \hat{r}_{ij}\) is the cosine of the angle between the instantaneous orientation of a reference molecule \(i\) and the unit vector connecting its center of mass to that of another molecule \(j\) as time passes [see Fig. 1]. Because of this definition, \(\eta_{ij}(t + \tau)\) is a measure of the relative orientation of a molecular pair at time \(t + \tau\) given that its orientation at time \(t\) is \(\eta_{ij}(t)\). Therefore, \(\sigma(\tau) \to 1\) as \(\tau \to 0\) in agreement with plots in Figs. 10(a) and 10(b) for various temperatures and pressures. At sufficiently low \(P_1\), \(\sigma(\tau)\) eventually decays with increasing time. The decay is delayed more as the nature of the liquid-crystalline phase changes in the direction \(I \to N \to \text{sm-A}\), that is, with increasing \(P_1\) [see Fig. 10(a)].

One also notices from Fig. 10(a) that decorrelation of relative orientations becomes very slow as soon as one enters the RN phase. This is already evident from the plot for \(P_1 = 2.3\) immediately after the sm-A-RN phase transition has occurred (see Fig. 4). However, the corresponding plot in Fig. 10(a) shows that \(\sigma(\tau)\) eventually decays at long times. This is apparently not so at the higher pressure \(P_1 = 2.8\) in the RN phase. The relevant plot in Fig. 10(a) shows only a weak decay of \(\sigma(\tau)\) over an intermediate time range \(1 \lesssim \tau \lesssim 10\) and then remains nearly constant for longer times \(\tau > 10^3\). The shape of \(\sigma(\tau)\) seems to reflect a two-stage decorrelation process involving those conformations represented by the bimodal distribution \(P(r^+)\) plotted in Fig. 9(a). In fact, intuitively it seems sensible to assume that decorrelation during the intermediate time interval is associated with the orientational dynamics of shifted side-side conformations depicted in Fig. 8(a). These conformations are expected to be less stable than the stringlike ones depicted in Fig. 8(b). This notion is further corroborated by the slowing down of the dynamics at longer times with increasing \(P_1\), which causes the population of stringlike conformations to increase according to plots in Figs. 9. This qualitative picture remains unaltered at the higher \(T = 6.0\) as parallel plots in Fig. 10(b) show. However, at this temperature the sm-A phase is absent in agreement with our earlier analysis of various structural quantities.
From the discussion of orientational relaxation one may get the impression that the RN phase is rather sluggish with respect to its dynamics. While this is certainly true for the rotational dynamics, it turns out that mass transport is actually quite fast in the RN phase. A suitable measure of mass transport is the mean-square displacement (MSD) of molecules. It measures the on-average net distance a molecule’s center of mass is able to travel in a given amount of time. Because of the large degree of nematic order characteristic of the RN phase it seems sensible to introduce a specialized MSD by considering displacements of molecules in the direction of their long axes. Specifically, we define \( r_i^\parallel \equiv \hat{u}_i \cdot r_i \) such that the associated MSD for the displacement of molecules in the direction of their long axes may be cast as

\[
\langle (\Delta r^\parallel(t))^2 \rangle_i = \frac{1}{N} \left( \sum_{i=1}^{N} (r_i^\parallel(t + \tau) - r_i^\parallel(t))^2 \right).
\]

Plots in Fig. 11 illustrate the variation of the MSD with time on a double-logarithmic scale. At short times \( \tau \ll 10^{-1} \) MSDs for various phases collapse onto a single curve. In this regime, known as the ballistic regime, the MSD increases proportionally to \( \tau^2 \). In the ballistic regime molecules travel freely; that is, for sufficiently short times interactions with neighboring molecules are inconsequential. Therefore, the specific nature of the phase under study does not matter such that the MSDs for different phases become indistinguishable and can be represented by a unique curve.

At sufficiently long times, however, the motion of molecules becomes diffusive, that is, \( \langle (\Delta r^\parallel(t))^2 \rangle_i \propto \tau \). In the diffusive regime intermolecular interactions do, of course, matter greatly, unlike in the ballistic regime. Therefore, in the diffusive regime plots in Figs. 11(a) and 11(b) cannot be represented by a single curve but differ between I, N, sm-A, and RN phases. An inspection of the MSD for the sm-A phase reveals that ballistic and diffusive regimes are separated by a third, subdiffusive regime in which \( \langle (\Delta r^\parallel(t))^2 \rangle_i \propto \tau^{\alpha(t)} \), where \( 1 \lesssim \alpha(t) \lesssim 2 \) varies continuously. The crossover region of subdiffusive behavior reflects the presence of smectic layers because \( \langle (\Delta r^\parallel(t))^2 \rangle_i \) is a measure of mass transport in a direction normal to the layer plane [see Fig. 5(b)]. Diffusive motion of molecules out of their original smectic layer into a neighboring one is inhibited by the compactness of the layered structure. However, within each layer there is sufficiently little order such that molecules may eventually move from their original into a neighboring layer. This process demarcates the onset of ordinary diffusive motion. Depending on the local compactness of the smectic layers it may take some molecules longer than others before they exhibit diffusive motion, and this is the reason why the subdiffusive regime is characterized by a constant change in the time dependence of the MSD characterized by the exponent \( \alpha(t) \).

As a quantitative measure of mass transport in the diffusive regime it is convenient to introduce the self-diffusion coefficient \( D_\parallel \) via the expression

\[
D_\parallel = \lim_{\tau \to \infty} \frac{1}{2\tau} \langle (\Delta r^\parallel(t))^2 \rangle_i,
\]

which corresponds to the long-time slope of the MSDs plotted in Fig. 11. From that definition and the plots in Fig. 11 one immediately anticipates a self-diffusion coefficient which is largest in the RN phase compared with the other three phases. In fact, the plot in Fig. 12 shows a dramatic increase of \( D_\parallel \) as one enters the RN phase, whereas lower-pressure (I, N, or sm-A) phases exhibit rather small self-diffusivity. In particular, the sm-A phase is characterized by nearly vanishing self-diffusion constants which can be rationalized as above where we argued that the relatively compact layered structure makes it difficult for molecules to diffuse out of their original layer and penetrate into a neighboring one. The dramatic increase in mass transport in the direction of \( \hat{n} \) in combination with nearly perfect nematic order prompted us to refer to liquid crystals in the RN phase as “supernematics” [28].

More detailed insight into the dynamics of mass transport in the RN phase can be gained by also considering the MSD for perpendicular displacements of the molecules’ long axes [50] to which we refer as \( \langle (\Delta r^\perp(t))^2 \rangle_i \) by analogy with Eq. (20), where, of course, we replace \( r_i^\parallel \) by its counterpart \( r_i^\perp \equiv r_i - (\hat{u}_i \cdot r_i)\hat{u}_i \). Plots of the root MSD for perpendicular versus parallel molecular displacements \( \Delta r^\perp \equiv \sqrt{\langle (\Delta r^\perp(t))^2 \rangle_i} \) in Fig. 13 reveal that dynamically distinct regimes exist. In the ballistic regime the plot in Fig. 13 increases linearly with slope 1, which can be rationalized as follows. Over the relatively short times characteristic of the ballistic regime molecules move freely in space. Hence, their self-diffusion is largely controlled by the free volume surrounding a molecule. In the RN phase the shape of the free volume should be closely related to the shape of an individual spherocylinder. Therefore, rescaling \( \Delta r^\perp(t) \) by the aspect ratio \( \kappa \) and expressing \( \Delta r^\perp_{\perp}(t) \) in units of \( \sigma \) one anticipates the plot in Fig. 13 to increase linearly with a slope
In this paper we elucidate the connection between the formation of stringlike conformations of elongated molecules in the RN liquid-crystalline phase and enhanced self-diffusivity observed earlier by us \[28\] in these phases. We employ the RN liquid-crystalline phase and enhanced self-diffusivity formation of stringlike conformations of elongated molecules in a direction parallel to these axes in units of the aspect ratio \(\kappa\). Data correspond to the RN phase at \(T = 4.0\) and \(P = 2.6\). Solid line is a fit to guide the eye.

of 1 in the ballistic regime where both \(\Delta r_\perp(\tau)\) and \(\Delta r_\parallel(\tau)\) are small compared with \(\sigma\). If this condition does not hold any longer, intermolecular interactions begin to matter and self-diffusion is no longer ballistic. The plot in Fig. 13 shows that during the initial stage of nonballistic self-diffusion the plot of \(\Delta r_\perp(\tau)\) versus \(\Delta r_\parallel(\tau)\) levels off and reaches a plateau. During this stage molecules diffuse in stringlike conformations that remain intact, that is, the group of molecules forming a stringlike conformation stays together as an entity. However, if both \(\Delta r_\perp(\tau)\) and \(\Delta r_\parallel(\tau)\) are sufficiently larger than \(\sigma\), the plot in Fig. 13 increases again linearly but with a somewhat smaller slope of about 0.88 compared with the initial ballistic regime. Because in this second linear regime \(\Delta r_\perp(\tau)\) is of the order of several \(\sigma\) diffusive motion must involve the exchange of individual molecular units between neighboring supramolecular “strings,” which illustrates the complexity of the dynamics in the supernematic RN phase.

### IV. SUMMARY AND CONCLUSIONS

In this paper we elucidate the connection between the formation of stringlike conformations of elongated molecules in the RN liquid-crystalline phase and enhanced self-diffusivity observed earlier by us \[28\] in these phases. We employ a combination of MC and MD simulations performed in an isothermal-isobaric and in the microcanonical ensemble, respectively. Under conditions of confinement a sequence of mesophases is observed. These involve the more conventional I and N phases and, under suitable thermodynamic conditions, a sm-A phase. At higher pressures (densities) the more exotic RN phase may form, which is a nematic phase with surprisingly large nematic order and enhanced self-diffusivity in the direction of the nematic director \(\hat{n}\). Quantitatively, we express the extent of mass transport in terms of the self-diffusion coefficient \(D_1\). In the RN phase \(D_\parallel\) may exceed that characteristic of the I, N, and sm-A phases by up to an order of magnitude.

Our analysis of the underlying structure reveals that the RN phase is characterized by so-called strings, that is, groups of molecules arranged such that their long axes and their center-of-mass distance vectors point in the direction of \(\hat{n}\) with only very little deviation from a perfect arrangement. These arrangements can clearly be seen in representative “snapshots” of individual configurations. On the contrary, stringlike conformations are absent in the I, N, or sm-A phases. For the sm-A phase this may seem surprising at first on account of the formation of distinct layers in the direction of \(\hat{n}\). However, one has to bear in mind that in each individual layer the order of center-of-mass arrangements is still rather low, which apparently prevents the formation of strings between adjacent layers. The reader should also note that if one considers a single isolated string that remains intact indefinitely, one would anticipate \(\langle \Delta r_\perp^2(\tau) \rangle \propto \sqrt{\tau}\) characteristic of single-file diffusion \[51\]. In single-file diffusion the time dependence of the MSD is caused by the fact that particles cannot pass each other, a situation encountered experimentally for the motion of molecules in the narrow spaces existing in materials such as zeolites \[52\], single-wall carbon nanotubes \[53\], or colloids confined to one-dimensional channels \[54\]. However, in the present case one needs to realize that we are confronted with a totally different physical situation. As the “snapshots” of configurations show, many strings exist that are misaligned in the direction in which they diffuse. At sufficiently long times individual molecules are exchanged between neighboring supramolecular “stringlike” units. As a result, ordinary Fickian diffusion is observed in the limit of sufficiently long times.

The interesting question then becomes: Why is this diffusive motion enhanced? In fact, based upon plots of the equipotential surface, one would assume that even in a stringlike conformation molecules would “feel” most comfortable if individual members in two neighboring strings were perfectly aligned because of the energetically favored side-side arrangement of pairs of molecules. If this were the case, one would expect self-diffusion in the direction of the stringlike conformations to actually be slowed rather than enhanced on account of restoring forces acting in the direction of \(\hat{n}\) that pull molecules back to relative arrangements corresponding to locations of potential minima. However, this rationale ignores the fact that RN phases form at relatively high pressures at which individual strings are “squeezed” together in the direction perpendicular to the plane of the solid substrates. That strings are actually squeezed in that direction is reflected by the local density, which shows that in the RN phase one additional layer of molecules can be accommodated compared with either N or sm-A phases at lower pressures. In other words, molecules in neighboring strings are pushed toward each other. This happens to an extent such that the attractive interactions between any pair of molecules pertaining to different strings (and therefore the restoring forces in the direction of \(\hat{n}\)) are overcome at least partly. In other words, the average distance \(r^{-}\) between the molecules of a pair decreases with \(P_\parallel\) such that the pair slowly “climbs up” the repulsive part of the fluid-fluid interaction potential. Thereby, the net attraction between the two molecules is reduced, as revealed by the shift of the taller
maximum of $P(r^\perp)$ plotted in Fig. 9. As a result diffusion in stringlike conformations is enhanced rather than diminished.

This mechanism is similar to one proposed for mass transport in zeolites. For example, based upon experiments using quasi-elastic neutron scattering and corresponding MD simulations, Borah et al. could demonstrate that in NaY zeolites severe confinement causes self-diffusivity to become maximum under geometrically favorable conditions [29]. This effect known as “levitation” is most pronounced if the narrow void in the zeolite is comparable to the optimum distance between a diffusing molecule and the pore wall, which is, of course, determined by the underlying fluid-wall interaction potential. If the width of the void is either too small or too large, self-diffusivity is lower than under the optimum confinement conditions. Levitation is quite regularly observed in zeolites of various kinds (see Ref. [29] and references therein).

At this point one may ask: Is there any experimental evidence supporting the enhanced self-diffusion that we observe in our simulations? The dynamics of the RN phase has perhaps been studied most extensively by NMR. Even though the focus of these measurements was not directly on determining self-diffusion, some of the experimental observations are in reasonable agreement with our simulations. It is possible, for example, to extract longitudinal relaxation rates from data for the N and RN phase presented in Ref. [25]. In the RN phase these relaxation rates are considerably lower than those characteristic of the N phase. At the same $T$, these relaxation rates can be converted into correlation times that are significantly shorter in the RN as opposed to the N phase. However, it remains somewhat speculative to conclude that the reduced correlation times indicate that mass transport is enhanced in the RN phase as long as self-diffusion has not been identified as the underlying dynamical process.

Interestingly, some 30 years ago Ratna et al. [27] presented measurements of the electrical conductivity at the sm-A-RN phase transition for a pure liquid crystal and a mixture. These authors measured the ratio of electric conductivity in directions parallel and perpendicular to the optic axis. As one approaches the RN from the sm-A phase, this ratio increases dramatically [27]. These results for the pure compound can be interpreted as direct evidence of enhanced molecular mobility upon approaching the RN phase. Unfortunately, a similar conclusion may not apply to binary mixtures.

What would be needed at this stage is a direct measurement of translational self-diffusion. This is possible, for example, with pulsed field gradient NMR (PFG NMR) [55]. The diffusion tensor upon entering the N phase [56] was directly measured, and it was found that diffusivity along the molecular long axes increases with increasing nematic order. Similarly, n-alkanes in nanochannels diffuse more as the orientational order grows [57]. These observations are consistent with our predictions. However, to directly measure effects such as the one discussed in this work more sophisticated experimental techniques such as PFG NMR with magic angle spinning would be required. This state-of-the-art method has recently been shown to open new avenues of investigation. For example, Romanova et al. [58] showed that one may measure diffusion in liquid crystals confined to nanopores.

ACKNOWLEDGMENTS

We thank Jörg Käger (Universität Leipzig) for his hospitality and fruitful discussions. We are also grateful to Lorenzo Guiducci (Max-Planck-Institut für Kolloid- und Grenzflächenforschung Potsdam-Golm) for bringing Ref. [30] to our attention and thank the International Graduate Research Training Group 1524 “Self-assembled soft-matter nanostructures at interfaces” for financial support.

APPENDIX: THEORETICAL BACKGROUND

From a statistical physical perspective the partition function $Q$ of the canonical ensemble is a key quantity as far as equilibrium systems are concerned. More specifically, it can be demonstrated that with a proper choice of phase space variables, $Q$ for linear molecules can be written as [34]

$$Q = \frac{1}{\Lambda_{th}^{5N}} \frac{T}{m}^N Z,$$

(A1)

where $\Lambda_{th} = h/\sqrt{2\pi mk_bT}$ is the thermal de Broglie wave length,

$$Z = \frac{1}{2^N N!} \int \int \exp[\beta U(R, \hat{U})] dR d\hat{U}$$

(A2)

is the configuration integral of a system of $N$ indistinguishable molecules, and $\beta = 1/k_B T$ ($k_B$ Boltzmann’s constant, $T$ temperature). The factor $1/2^N$ in Eq. (A2) corrects for double counting equivalent configurations. These arise because of the head-tail symmetry of the molecules, that is, the equivalence of orientations specified by $\hat{u}_i$ and $-\hat{u}_i$. For the isothermal-isobaric ensemble employed in the MC simulations of this work

$$\Delta = \sum_{(s_x, s_z)} \exp(-\beta P_I A_{s_z}) Q$$

(A3)

is the relevant partition function [47]. It is then straightforward to show that the Gibbsian potential [47]

$$\mathcal{G} = -k_B T \ln \Delta$$

(A4)

is the relevant thermodynamic potential such that thermodynamic equilibrium is attained if $\mathcal{G}$ is minimum at any fixed values of $N$, $P_I$, $T$, and $s_z$. However, it should be noted that as far as static properties are concerned, the specific choice of $m$ or $I$ does not matter [47].

However, as far as the temporal evolution of the system is concerned, the specific choice of both $m$ and $I$ does matter. To see this, let us derive the equations of motion that govern the temporal evolution in a system of linear molecules. Starting from Hamilton’s equation of motion the translation of the molecular centers of mass is described by

$$r_i = v_i,$$

(A5a)

$$v_i = \frac{f_i}{m}, \quad i = 1, \ldots, N,$$

(A5b)

where $v_i$ and $f_i = -\nabla_i U$ are velocity and total force acting on the center of mass of molecule $i$. Similarly, one may derive equations of motion for the rotation of a molecule
starting again from Hamilton’s equations but this time taking angular velocity $\mathbf{\omega}$, and $\mathbf{u}_i$ as the conjugate canonical variables rather than linear momentum and center-of-mass position as in the derivation of Eqs. (A5). The resulting expressions are given by

$$\mathbf{\hat{u}}_i = \mathbf{\omega} \times \mathbf{u}_i, \quad (A6a)$$

$$\mathbf{\omega} = \frac{\tau}{I}, \quad i = 1, \ldots, N, \quad (A6b)$$

where $L = I\mathbf{\omega}$ [see Eq. (1)],

$$\tau_i \equiv \mathbf{u}_i \times g_i = \mathbf{\hat{u}}_i \times g_i^\perp \quad (A7)$$

is the torque acting on each molecule, and, following Fincham [59], $g_i \equiv -V_{ii} \mathbf{u}_i$ is the so-called gorque. The gorque may be thought of as a turning “force” that effects changes in molecular orientation. For linear molecules obviously only the gorque $g_i^\perp$ perpendicular to the molecular axis matters. It is obtained through the projection of $g_i$ onto $\mathbf{u}_i$, via

$$g_i^\perp = g_i - (g_i \cdot \mathbf{u}_i) \mathbf{u}_i. \quad (A8)$$

Moreover, in the case of linear molecules the angular velocity must always be perpendicular to the molecular axis, that is, $\mathbf{\omega} \cdot \mathbf{u}_i = 0$. This makes it convenient to replace the angular by the orientational velocity $\mathbf{\omega}_i$ such that Eqs. (A6) can be replaced by the equivalent but, from a numerical perspective, much more convenient equations

$$\mathbf{\hat{u}}_i = \mathbf{\omega}_i, \quad (A9a)$$

$$\mathbf{\omega}_i = \frac{g^\perp_i}{I} = -w^2\mathbf{\hat{u}}_i, \quad i = 1, \ldots, N. \quad (A9b)$$

The derivation of Eqs. (A9) requires a little bit of extra but straightforward vector algebra [59]. Finally, Eqs. (A5) and (A9) show that $m$ and $I$ determine the time scale of translational and rotational motion, respectively.


