Long-time relaxation dynamics in nematic and smectic liquid crystals of soft repulsive colloidal rods

DOI:
10.1103/PhysRevE.105.014703

Document Version
Accepted author manuscript

Link to publication record in Manchester Research Explorer

Citation for published version (APA):
Cywiak, D., Gil-villegas, A., & Patti, A. (2022). Long-time relaxation dynamics in nematic and smectic liquid crystals of soft repulsive colloidal rods. Physical Review E, 105(1). Advance online publication. https://doi.org/10.1103/PhysRevE.105.014703

Published in:
Physical Review E

Citing this paper
Please note that where the full-text provided on Manchester Research Explorer is the Author Accepted Manuscript or Proof version this may differ from the final Published version. If citing, it is advised that you check and use the publisher's definitive version.

General rights
Copyright and moral rights for the publications made accessible in the Research Explorer are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

Takedown policy
If you believe that this document breaches copyright please refer to the University of Manchester’s Takedown Procedures [http://man.ac.uk/04Y6Bo] or contact uml.scholarlycommunications@manchester.ac.uk providing relevant details, so we can investigate your claim.

Download date: 26. Oct. 2023
Long-time relaxation dynamics in nematic and smectic liquid crystals of soft-repulsive colloidal rods

Daniela Cywiak* and Alejandro Gil-Villegas†

Division de Ciencias e Ingenierías, Universidad de Guanajuato, Campus León, México

Alessandro Patti‡

Department of Chemical Engineering and Analytical Science, University of Manchester, United Kingdom

(Dated: December 1, 2021)

Understanding the relaxation dynamics of colloidal suspensions is crucial to identify the elements that influence the mobility of their constituents, assess their macroscopic response across the relevant time and length scales, and thus disclose the fundamentals underpinning their exploitation in formulation engineering. In this work, we specifically assess the impact of long-ranged ordering on the relaxation dynamics of suspensions of soft-repulsive rod-like particles, which are able to self-organise into nematic and smectic liquid-crystalline phases. Rods are modelled as soft repulsive spherocylinders with length-to-diameter ratio $L_s = 5$, interacting via the truncated and shifted Kihara potential. By performing Dynamic Monte Carlo simulations, we analyse the effect of translational and orientational order on the diffusion of the rods along the relevant directions imposed by the morphology of the background phases. To provide a clear picture of the resulting dynamics, we assess their dependence on temperature, which can dramatically determine the response time of the system relaxation and the self-diffusion coefficients of the rods. The computation of the van Hove correlation functions allows us to identify the existence of rods that diffuse significantly faster than the average and whose concentration can be accurately adjusted by a suitable choice of temperature.

I. INTRODUCTION

The study of the dynamical properties of colloidal suspensions has generated an exceptional insight into multiple fields of science and technology, shedding light on processes such as self-assembly and nucleation [1], and systems, such as active matter [2] and liquid crystals (LCs) [3–5], whose key mechanisms are dramatically influenced by the particle dynamics over time. The relatively recent development of experimental techniques for the synthesis of a fascinating spectrum of particle shapes [6] has boosted the interest in extending to anisotropic particles methods predominantly used to study dynamic arrest and glass transition in suspensions of spherical particles [7]. These methods include the use of hard-core models to mimic the essential features of a spectrum of colloidal systems, including LCs. As Onsager demonstrated in his seminal theory, these relatively simple models are indeed able to predict the isotropic-to-nematic transition of infinitely long rod-like particles, as later on verified by computer simulation [8, 9]. Nevertheless, Van der Waals and long-range electrostatic forces modify the phase diagram and introduce important effects in the thermodynamic and structural properties of these systems, particularly in the location of phase boundaries, such as isotropic-nematic and nematic-smectic transitions [10, 11].

A wide variety of hard- and soft-core models have been used to gain a better insight into the behavior of thermotropic (molecular) and colloidal LCs [12]. In the case of spherical particles, Medina-Noyola and coworkers demonstrated that structural properties and diffusion coefficients of spheres interacting with a repulsive Sutherland potential can be mapped onto the corresponding properties of hard-sphere (HS) systems, using effective diameters dependent on density and temperature [13, 14]. More recently, Jackson and coworkers obtained an effective soft-repulsive potential based on the Mie model in order to reproduce structural properties of the HS system [15], a procedure that has been extended to square-well potentials [16] and applied successfully in molecular simulations of colloidal systems [17]. The approach of using potential models with soft repulsive and attractive interactions of variable range, such as the Mie model for chain molecules [18, 19], have had important implications in the prediction of a wide variety of phase diagrams for molecular fluids [20].

When investigating the dynamics of hard-core particles, the usual simulation techniques of choice, namely Molecular dynamics (MD) and Brownian dynamics (BD), cannot be directly applied, as the form of the interaction potential does not allow one to integrate the equations of motion. Additionally, while MD can accurately reproduce the deterministic dynamics of atoms and molecules, it is not suitable to mimic the Brownian motion of colloids unless both dispersed and continuous phases are explicitly incorporated, resulting in a very computationally demanding system to study. On the other hand, BD relies on stochastic equations of motion that implicitly incorporate the presence of a solvent, but faces, along with MD, the limitation of an integration time-step that should be sufficiently small to guarantee precision at the cost of missing the long-time relaxation dynamics. This is not a major problem in sufficiently

* d.cywiak.cordova@ugto.mx
† gil@fisica.ugto.mx
‡ alessandro.patti@manchester.ac.uk
dilute colloidal suspensions, but it is indeed a challenge in
dense colloids, including LCs, whose structural relax-
ation completely unfolds over relatively long time scales.
These limitations can be bypassed by the Dynamic Monte
Carlo (DMC) method, which is able to capture the Brow-
nian dynamics of colloids without employing stochastic
or deterministic equations of motion. Based on the stan-
ard Metropolis algorithm [21], DMC can quantitatively
and qualitatively reproduce BD simulation results in the
limit of small displacements [22–29].

In this work, we apply the DMC method to study the
dynamics of nematic (N) and smectic (Sm) LCs of col-
oil rod-like particles. Rods are here represented as
soft repulsive spherocylindrical (SRS) particles interact-
ing via the Kihara potential, which has been used in the
past to investigate the behavior of prolate [30, 31] and
oblate [32] spherocylinders. We stress that the present
manuscript does not contain further developments of the
already established DMC simulation technique and the
reader is referred to former works for details [24–29]. W e
already established DMC simulation technique and the
manuscript does not contain further developments of the

This paper is organised as follows. In Section II, we
describe the SRS model, provide the main details of the
DMC simulation method applied in this work and intro-
duce the observables calculated to characterize the dy-
namics in N and Sm LCs and its dependence on long-
range ordering and temperature. In Section III, we dis-

cuss the ability of SRS to diffuse in these LC phases and
the structural relaxation of the systems over time. Fi-
nally, we draw our conclusions in Section IV.

II. MODEL AND SIMULATIONS

As mentioned above, colloidal rods are here modelled
as SRS particles interacting via the Kihara potential. In
particular, we studied systems of \( N_r = 1000 \) prolate spher-
ocylinders of length-to-diameter ratio \( L^* \equiv L/\sigma = 5 \),
where \( L \) and \( \sigma \) are, respectively, the length and diame-
ter of a cylindrical body capped by two hemispheres of
identical diameter. The total length of the rod is thus
\( L + \sigma \). The interaction between particles is described by
a repulsive, truncated and shifted Kihara potential that
reads

\[
U_{ij} = \begin{cases} 
4\epsilon \left[ \left( \frac{a}{d_m} \right)^{12} - \left( \frac{a}{d_m} \right)^{6} + \frac{1}{4} \right] & \text{d}_m \leq \sqrt[3]{2}\sigma \\
0 & \text{d}_m > \sqrt[3]{2}\sigma
\end{cases},
\]

where \( U_{ij} = U_{ij}(\mathbf{r}_{ij}, \mathbf{u}_i, \mathbf{u}_j) \). The subscripts \( i \) and \( j \) refer
to a pair of interacting spherocylinders, \( \mathbf{r}_{ij} \) is the
centre-to-centre distance between them, \( \epsilon \) their interac-
tion strength, \( \mathbf{u}_i \) and \( \mathbf{u}_j \) indicate the particles' ori-
tentation, and \( d_m = d_m(\mathbf{r}_{ij}, \mathbf{u}_i, \mathbf{u}_j) \) is the minimum distance
between \( i \) and \( j \). The interested reader is referred to Ref. [33]
for additional details on the computation of the minimum
distance between prolate spherocylinders. All
simulations have been performed in the canonical ensem-
ble at constant number of particles, temperature (\( T \))
and volume (\( V \)). N and Sm phases have been simulated in
cubic boxes with periodic boundary conditions of size
\( L_x = L_y = L_z = 20.27\sigma \) and \( L_x = L_y = 19\sigma \) and
\( L_z = 18\sigma \), respectively. The density, \( \rho \), of N and Sm
phases was set according to the phase diagrams of Ki-
harah spherocylinders reported in Ref. [31]. In particular,
\( \rho^*_N = 0.12 \) and \( \rho^*_Sm = 0.15 \) for N and Sm phases,
respectively, with \( \rho^* = N_\sigma^3/V \). To equilibrate N and Sm
phases at these values of density, we melted initial con-
fugurations of perfect crystals at the desired temperature
by performing standard MC simulations. In particular,
rotational and translational movements of randomly se-
lected particles were accepted or rejected according to the
Metropolis algorithm [21]. The systems were consid-
ered to be at equilibrium when the potential energy of
the system had reached a steady value within moderate
statistical fluctuations. More specifically, equilibration
runs took between \( 10^6 \) and \( 3 \times 10^6 \) MC cycles.

After equilibration, we performed DMC simulations to study the relaxation dynamics of N and Sm phases. In
DMC simulations, to realistically mimic the Brown-
ian motion of colloidal particles, unphysical moves, such
as swaps or cluster moves, are not performed. An in-
sightful description of the DMC method applied in this
work is available elsewhere [24–29]. Here we only pro-
vide a brief overview of the main features of the method
and refer the interested reader to these works for details.
DMC simulations were performed in N and Sm phases
at scaled temperatures \( T^* = 5, 8, 10, 12, 15 \) and 20, with
\( T^* = k_B T/\epsilon \) and \( k_B \) the Boltzmann constant. We
selected \( \sigma \), \( \epsilon \) and \( \tau = \sigma^2/D_0 \) as units of length, energy
and time, respectively, where \( D_0 = k_B T/\mu \sigma \) is a diffu-
sion constant and \( \mu \) the viscosity of the implicit solvent.

One DMC cycle consists of \( N_r \) attempts of simultane-
ously displacing and rotating a randomly selected par-
ticle. These moves are accepted according to the prob-
ability min[1, \exp(\Delta U/k_B T)], where \( \Delta U \) is the energy
difference between new and old configurations. The mag-
nitude of elementary displacements and rotations is de-
fined according to the Einstein equations and the particle
diffusion coefficients at infinite dilution. More specifi-
cally, displacements in the direction of \( \mathbf{u}_i \) and perpen-
dicular to it where randomly selected from uniform distri-
butions that satisfy the conditions \( |X_\parallel| \leq \sqrt{2D_\parallel \delta_{MC}} \) and
\( |X_\perp| \leq \sqrt{2D_\perp \delta_{MC}} \), respectively, where \( \delta_{MC} \)
is the arbitrarily set MC time step, while \( D_\parallel \) and \( D_\perp \)
correspond to the translational diffusion coefficients at in-
finite dilution along \( \mathbf{u}_i \) and perpendicularly to it, respec-
tively. A similar approach was used to calculate particle rotations, where the vector \( \mathbf{u}_i \) changes to \( \mathbf{u}_i + \delta \mathbf{u}_i \), with \( \delta \mathbf{u}_i = Y_{\varphi,1} \mathbf{w}_{j,1} + Y_{\varphi,2} \mathbf{w}_{j,2} \). The two randomly chosen vectors \( \mathbf{w}_{j,m} \) are perpendicular to each other and to \( \mathbf{u}_i \). Finally, \( Y_{\varphi,1} \) and \( Y_{\varphi,2} \) are random numbers selected from uniform distributions that satisfy the condition \( |Y_{\varphi,m}| \leq \sqrt{2D_\varphi \delta t_{MC}} \) where \( D_\varphi \) is the rotational self-diffusion coefficient of the rod.

Translational and rotational diffusion coefficients of rod-like particles at infinite dilution have been estimated by applying the analytical expressions based on the induced-forces method by Bonet Avalos and coworkers [34]. In particular:

\[
D_\perp = \frac{\ln(2/\gamma) - 1/2 - I^{tt}}{2\pi/\gamma} \quad (2)
\]
\[
D_\parallel = \frac{\ln(2/\gamma) - 3/2 - I^{tt}}{\pi/\gamma} \quad (3)
\]
\[
D_\varphi = \frac{3\ln(2/\gamma) - 11/6 - I^{rr}}{\pi \sigma^2 / (2\gamma)^3} \quad (4)
\]

where \( 1/\gamma = 2(L^* + 1) \), \( I^{tt} \equiv \frac{1}{2} \int_1^1 dx \ln h(x) \), \( I^{rr} \equiv \frac{3}{2} \int_1^1 dx x^2 \ln h(x) \) and \( h(x) = (1-x^2)^{1/2n} \). The function \( h(x) \), applied to model particles with revolution symmetry, approximates very well the shape of a spherocylinder when \( n = 8 \). Under these conditions, \( I^{tt} \approx -0.0061 \) and \( I^{rr} \approx -0.017 \). The translational and rotational diffusion coefficients at infinite dilution used in our DMC simulations are given in Table I for different values of the reduced temperature. We note that the value of the three sets of diffusion coefficients are different from those employed in Ref. [24], especially so at \( T^* = 20 \). Such difference is due to the fact that Ref. [24] made use of the analytical expressions available for prolate spheroids, whose geometry is roughly similar, but not identical to that of spherocylinders.

| \( T^* \) | \( D_\parallel / D_0 \) | \( D_\perp / D_0 \) | \( D_\varphi / D_0 \) |
|---|---|---|---|
| 5 | 0.223 | 0.177 | 0.029 |
| 8 | 0.357 | 0.284 | 0.047 |
| 10 | 0.446 | 0.355 | 0.059 |
| 12 | 0.536 | 0.427 | 0.071 |
| 15 | 0.670 | 0.533 | 0.089 |
| 17 | 0.759 | 0.605 | 0.101 |
| 20 | 0.893 | 0.711 | 0.119 |

In order to obtain the actual time scale for Brownian dynamics, we have rescaled the MC timescale via the acceptance rate using the following relation

\[
t_{BD} = \frac{A}{3} C_{MC} \delta t_{MC} \quad (5)
\]

where \( t_{BD} \) is the Brownian time after \( C_{MC} \) MC cycles, \( A \) is the average acceptance rate over this number of cycles and \( \delta t_{MC} \) the corresponding MC time. This result allows one to rescale the dynamical properties and consistently compare the structural relaxation of N and Sm phases across the spectrum of temperatures studied here. More specifically, we evaluated the mean-squared displacement (MSD), the self-part of the Van Hove correlation function (s-VHF) and the self-part of the intermediate scattering function (s-ISF). Each of these functions has been calculated in the direction of the nematic director and in planes perpendicular to it. The number trajectories used to obtain accurate statistics was approximately 100. In particular, the parallel and perpendicular MSD read

\[
\langle \Delta r^2_i(t) \rangle = \frac{1}{N_r} \left\langle \sum_{j \neq i} \left[ (r_j(t) - r_j(0)) \cdot \mathbf{n} \right]^2 \right\rangle \quad (6)
\]
\[
\langle \Delta r^2_i(t) \rangle = \frac{1}{N_r} \left\langle \sum_{j \neq i} \left[ (r_j(t) - r_j(0)) \times \mathbf{n} \right]^2 \right\rangle \quad (7)
\]

where \( \langle \ldots \rangle \) denotes ensemble average and \( \mathbf{n} \) is the nematic director. Similarly, the pair distribution functions parallel and perpendicular to the director are given by

\[
g_\parallel(z) = \frac{1}{N_r^2} \left\langle \sum_{i \neq j} \delta(\mathbf{r}_i - \mathbf{r}_j) \cdot \mathbf{n} \right\rangle \quad (8)
\]
\[
g_\perp(r) = \frac{1}{N_r^2} \left\langle \sum_{i \neq j} \delta(\mathbf{r}_i - \mathbf{r}_j) \times \mathbf{n} \right\rangle \quad (9)
\]

where \( z \) and \( r \equiv \sqrt{x^2 + y^2} \) are the particle center-to-center distances in the direction of \( \mathbf{n} \) and perpendicular to it, respectively, and \( \delta \) is the Dirac delta function. Additionally, the probability distribution of the particles at time \( t_0 \), given by the self-part of the van Hove Function, reads

\[
G_s(z,t) = \frac{1}{N_r} \left\langle \sum_{j=1}^N \delta(z - [z_j(t + t_0) - z_j(t_0)]) \right\rangle \quad (10)
\]
\[
G_s(r,t) = \frac{1}{N_r} \left\langle \sum_{j=1}^N \delta(r - [r_j(t + t_0) - r_j(t_0)]) \right\rangle \quad (11)
\]

The s-VHFs provide insight into the presence of particles that are significantly slower or faster than the average particle over the same time scale. This scenario is not necessarily the same in the direction of the nematic director and perpendicularly to it. Finally, the s-ISF gives a measure of the structural relaxation of the system over time and quantifies the decay of its density fluctuations. As noticed for the s-VHFs, this behavior is not expected
to be isotropic. In this case, we also estimate the parallel and perpendicular contributions as follows

\[
F_{s,z}(t) = \frac{1}{N_r} \left( \sum_{j=1}^{N_r} \exp[i \mathbf{q} \cdot (\mathbf{r}_j(t + t_0) - \mathbf{r}_j(t_0))] \cdot \mathbf{n} \right) \tag{12}
\]

\[
F_{s,xy}(t) = \frac{1}{N_r} \left( \sum_{j=1}^{N_r} \exp[i \mathbf{q} \cdot (\mathbf{r}_j(t + t_0) - \mathbf{r}_j(t_0)) \times \mathbf{n}] \right) \tag{13}
\]

where the wave vector \( \mathbf{q} = \mathbf{q}_\parallel + \mathbf{q}_\perp \) is defined at the main peaks of the static structure factor, taking values of \( |\mathbf{q}_\parallel| \sigma \simeq 1 \) and \( |\mathbf{q}_\perp| \sigma \simeq 6 \) for the parallel and perpendicular components with respect to the director, respectively.

III. RESULTS

Before presenting and discussing the relevant observations on the dynamics of SRS rods in N and Sm phases, we first analyse the structural properties that help us distinguish between positionally and merely orientationally ordered phases. To this end, we computed the pair-correlation functions \( g_\perp(r) \) and \( g_\parallel(z) \), shown in Figs. 1 and 2, respectively. The former can be considered as an in-layer pair-correlation function for the case of Sm phases, where positional ordering in the direction of \( \mathbf{n} \) exists. Our results indicate the existence of a typical fluid-like behavior in the perpendicular direction of both N and Sm phases, with the first peak occurring at a distance of approximately one diameter length and the amplitude of oscillations decaying exponentially to 1 at relatively short distances. Upon increasing temperature from \( T^* = 5 \) to 20, all peaks tend to flatten and fluctuations decay at progressively shorter distances. As far as the parallel pair correlation function, \( g_\parallel(z) \), is concerned, the pronounced periodic correlations of Fig. 2 confirm the layered structure typically observed in Sm LCs. In particular, the position of each peak roughly corresponds to the location of each smectic layer, where particle density is maximal. By contrast, the inter-layer spacing is almost completely empty, the probability of observing particles in between layers being very low. Increasing temperature has a significant effect on the density distribution in the Sm phase, but a practically negligible effect in the N phase, which shows no evidence of positional order at all temperatures studied.

Having established the structural differences between the N and Sm phases studied here, we now investigate how these distinctive morphological attributes can in turn determine distinct dynamical signatures. To start with, we first estimated the MSD in the direction parallel to the nematic director and calculated the long-time diffusion coefficients. To this end, we ran DMC simulations at different values of the MC time step, between \( \delta t_{MC}/\tau = 10^{-5} \) and \( 10^{-2} \), and then applied Eq. (5) to rescale the results and recover the unique BD time scale \([24]\). The rescaled MSDs collapse into a single master curve as shown in Fig. 3, where we report the parallel MSD in the Sm phase at \( T^* = 10 \). The re-scaling procedure to obtain the MSD across the whole spectrum of relevant time scales is the same for all the remaining systems. The resulting master curve has been obtained by superimposing four separate rescaled MSDs (dashed lines) calculated over DMC simulations at \( \delta t_{MC}/\tau = 10^{-5}, 10^{-4}, 10^{-3} \) and \( 10^{-2} \). The so-calculated MSD exhibits an initial diffusive regime, mostly deter-
mined by the particle geometry, followed by an intermediate time regime where the presence of neighboring layers, forming a sort of cage around the particles, slows down diffusion and, finally, a long-time diffusive regime that fully develops at $t/\tau > 1$. Very similar tendencies have also been detected at $T^* = 5, 8, 12, 15$ and 20, with some differences observed in the extension of the cage effect and the onset of the long-time diffusive regime. In particular, the effect of temperature on the MSD is clarified in Fig. 4, where we report parallel and perpendicular MSDs in N (top frame) and Sm (bottom frame) LCs at $T^*=5$ and 20, that is the lowest and highest temperatures studied. For the sake of clarity, we do not show the parallel and perpendicular MSDs at intermediate temperatures, which exhibit a profile in between those reported in Fig. 4 for N and Sm phases. We also notice that, in the N phase, at short time scales the relationship between parallel and perpendicular MSDs is such that $\xi \equiv \Delta r_{\parallel}^2/\Delta r_{\perp}^2 > 1$, while it inverts at intermediate time scales, when the parallel MSD becomes larger and stays so up to the long-time diffusive regime. This behavior has also been reported in Brownian dynamics simulations of SRS rods at $T^* = 1.465$ [35], a temperature at which the phase behavior of soft spherocylinders can be mapped on that of hard spherocylinders [31]. The dominant character of the long-time parallel diffusion has also been observed experimentally in N phases of rod-like viruses [36], but less clear is whether or not this tendency already exists at short time scales as observed in simulations. To gain an insight into the effect of temperature on the relative importance, over time, between the one-dimensional diffusion along $\mathbf{n}$ and the two-dimensional diffusion perpendicular to $\mathbf{n}$, we have calculated the time at which a crossover from $\xi > 1$ to $\xi < 1$ is observed. This time, referred to as inversion time and indicated with $t_i$, quantifies the time scale over which this crossover is produced in the N phase. Interestingly enough, $t_i$ changes with the temperature as shown in Fig. 5. In particular, we observe that $t_i$ is relatively large at low temperatures and then gradually decreases following an exponential law of the type $t_i/\tau = A + B \exp(-C T^*)$, where $A = 0.40, B = 1.51$ and $C = 0.37$ are fitting parameters. It is evident that at large enough temperatures, $t_i$ tends to a constant value, approximately equal to 0.40$\tau$, that will not change significantly up to the I-to-N transition temperature.

The MSDs are instrumental to calculate the long-time self-diffusion coefficients and their dependence on temperature. More specifically, parallel and perpendicular
self-diffusion coefficients in N and Sm phases were obtained from the slope of the corresponding MSDs in the long-time diffusive regime:

$$D_{\parallel,\perp} = \lim_{t \to \infty} \frac{1}{2l} \frac{d}{dt} \left\langle \sum [r_i(t) - r_i(0)]^2 \right\rangle$$  \hspace{1cm} (14)

where $l = 1$ or 2 denotes the dimensionality of particle dynamics associated to the parallel or perpendicular MSD, respectively. By contrast, the total self-diffusion coefficient has been calculated as $D_{Tot} = (D_{\parallel} + 2D_{\perp})/3$. The dependence of the self-diffusion coefficients on temperature in N and Sm phases is presented in the two frames of Fig. 7. In agreement with previous molecular dynamics simulation of rod-like molecular liquid crystals [37], we find that the three sets of long-time self-diffusion coefficients exhibit a dependence on $T^*$ that is well-described by an Arrhenius-like exponential law, that reads $D/D_0 \approx D^* \exp(-E^*/T^*)$, with the pre-exponential factor $D^*$ and activation energy $E^*$ fitting parameters. We also observe that the dependence of $D_{\perp}$ on temperature is very similar in both N and Sm phases. At a given temperature, most likely due to the packing difference between the two LC phases, the numerical value of $D_{\perp}$ is slightly larger in the N phase than in the Sm phase, but otherwise $D_{\perp} = D_{\perp}(T^*)$ exhibits the same exponential trend, with very similar fitting parameters, in both frames of Fig. 7. On the other hand, the diffusion along the director is significantly slower in the Sm phase ($E^* \approx 42$) than in the N phase ($E^* \approx 11$) by almost one order of magnitude, most likely due to the layered structure that hampers the penetration of the rods and thus delays their diffusion along the nematic director. These findings are in qualitative agreement with former theoretical, simulation and experimental works that clarified the existence of free-energy barriers hampering the diffusion of rod-like particles through Sm layers [38–43]. Therefore, while SRS particles in the N phase preferentially diffuse in the direction of the nematic director, in the Sm phase they are essentially constrained in a two-dimensional space, especially at $T^* < 10$, where $D_{\parallel}$ is almost negligible.

In the light of these considerations, we now turn our attention to the probability of observing particles that displace significantly shorter or longer distances than the average particles over the same period of time. The existence of such particles, here referred to as fast or slow, is corroborated by the computation of the s-VHFs along the nematic director and perpendicularly to it, as given, respectively, in Eqs. (10) and (11). To illustrate this, we show the s-VHFs at $t/\tau = 10^4$, a time that is sufficiently long to observe the relevant dynamical features of both N and Sm phases across the whole spectrum of temperatures studied. In particular, the parallel s-VHFs of Sm LCs, shown in the top frame of Fig. 7, display periodically peaked profiles that follow the typical layered structure of this phase. At increasing temperatures, from $T^* = 5$ to 20, these peaks become less and less pronounced, suggesting a more uniform probability of finding particles at any distance along the nematic director. Nevertheless, at relatively low temperature, with the smectic layers well-defined and less prone to density fluctuations, the profiles unambiguously suggest that particles preferentially jump from layer to layer and almost no particles are observed in between. For instance, at $T^* = 5$, while most particles are still in their original layer (primary peak), there exist especially fast particles that succeeded in diffusing, over the same period of time, to a contiguous layer (secondary peak). This is also observed at larger temperatures, but the difference between the height of primary and secondary peaks gradually softens and eventually disappears at $T^* = 20$. 

![Figure 6](image_url)

Figure 6. Total ($D_{Tot}$), parallel ($D_{\parallel}$) and perpendicular ($D_{\perp}$) self-diffusivities, represented with triangles, squares and circles, respectively, as a function of the reduced temperature in the N (a) and Sm (b) phases. Solid lines are exponential fits of the type $D/D_0 \approx D^* \exp(-E^*/T^*)$, with $D^* = \{0.0621, 0.0196, 0.0328\}$ and $E^* = \{11.5901, 12.1927, 11.6009\}$ for parallel, perpendicular and total self-diffusivities, respectively, for the nematic states, and $D^* = \{0.0308, 0.0167, 0.0129\}$ and $E^* = \{42.243, 12.1584, 12.948\}$ for parallel, perpendicular and total self-diffusivities, respectively, for the smectic states.
The bottom frame of Fig. 7 reports similar s-VHFs for the N phase. In this case, profiles with a maximum at $z = 0$ and monotonic decay at relatively long distances are observed. Most particles are therefore at or very close to their original position, with few of them fast enough to be displaced substantially larger distances over the same time window. With increasing temperature, more and more particles are able to move longer distances and, correspondingly, less and less are found at their original location. Finally, the perpendicular s-VHFs shown in Fig. 8 for N (bottom frame) and Sm (top frame) phases reveal the presence of an interesting variety of particles. At $t/\tau = 10^4$, most of them have left their initial position, as indicated by the peak of the distribution. These particles coexist with others that either remained very close to their original location or displaced significantly larger distances. Upon increasing temperature, the probability of observing such slow and fast particles becomes more and more uniform and would eventually become space-independent at very large temperatures, at which the system would transform into an isotropic phase.

Temperature also plays a key role in determining the time scale of the structural relaxation of the system. This has been estimated by computing the s-ISF in direction parallel and perpendicular to $n$. The s-ISFs of N and Sm phases are respectively shown in Figs. 9 and 10. In both cases, they have been calculated at the wave vectors corresponding to the peak of the static structure factor, which are $q = (0, 0, q_z)$, with $q_z \sigma = 1$ for parallel s-ISFs and $q = (q_x, q_y, 0)$ with $\sqrt{q_x^2 + q_y^2} \sigma = 6$ for perpendicular s-ISFs. Both LC phases exhibit a relevant difference between parallel and perpendicular relaxation, with the former taking up to 2 to 3 extra time decades. In all the cases studied, the decay of the s-ISFs closely follows a stretched-exponential function of the form $\exp\left[-(t/t_\tau)^\beta\right]$, typically observed in dense fluids [44], with $t_\tau$ and $\beta$ fitting parameters. In particular, the exponent $\beta$ is approximately between 0.6 and 0.7 for $F_{s,xy}$, and between 0.8 and 0.9 for $F_{s,z}$, suggesting a more stretched decay in planes perpendicular to the nematic director than in the direction parallel to it. These values agree well with those reported in previous simulation of hard spherocylinders [45, 46]. While the dependence of $\beta$ on temperature is relatively mild, the relaxation time $t_\tau$, defined as the time at which $F_s = 1/e$, changes significantly with the temperature as can be inferred from Fig. 11, where $\ln(t_\tau/\tau)$ is plotted as a function of $\ln(T^*)$. The so-calculated relaxation time exhibits a power-law dependence on $T^*$ that holds in both Sm and N phases.

IV. CONCLUSIONS

In summary, we have performed DMC simulations to investigate the dynamics of soft-repulsive rod-like particles in nematic and smectic LCs. To this end, we have calculated a spectrum of dynamical properties that helped us characterise the long-time relaxation decay in the direction of the nematic director and perpendicularly to it. In particular, the MSD was key to obtain the self-diffusion coefficients and gain an insight into their dependence on temperature, the s-VHF unveiled the existence of particles able to cover significantly longer distances than most of the particles over the same time, and the s-ISF clarified the timescales of the structural fluctuations’ decay. Our results suggest a similar fluid-like diffusive behavior in the direction perpendicular to the nematic director in both N and Sm phases. By contrast, the crystal-like arrangement of the Sm phase along the nematic director determines a significantly different dy-
The analysis of the s-VHFs in the direction of the nematic director suggests the presence of rods that are able to displace significantly longer distances than the average particle over the same time scale. While such fast particles are found in both the N and Sm phases, the probability distribution profiles of their parallel displacements in these phases are not the same. More specifically, periodically peaked s-VHFs are found in the Sm phases, with the peaks becoming smoother and smoother at increasing temperature. By contrast, in the N phase, no peaks are observed, but monotonically decreasing probabilities that vanish at sufficiently long distances. To some extent, the parallel s-VHFs of the N phase are very similar to those calculated perpendicularly to the nematic director, whose profiles in the N and Sm phases are almost completely indistinguishable. However, the perpendicular s-VHFs exhibit a maximum at relatively short distances that suggests the existence of especially slow particles that, even at sufficiently long times, have displaced less than one rod diameter from their original position. The simultaneous presence of slow and fast particles contributes to determin-
mine the structural relaxation of the systems, which has been assessed by calculating the s-ISF. As observed in dense liquids, the s-ISFs exhibit a stretched exponential decay, which can take up to 3 time decades more along the nematic director than in the directions perpendicular to it.

The dynamical properties of the soft repulsive model studied here can be extended to introduce other effects that are relevant for the characterization of soft matter phases, like polydispersity in viruses [5] and the introduction of electrostatic interactions in models for colloids and proteins [47]. Since the Mie-potential has extended the application of the Lenard-Jones model to describe properties of real substances [20], we can expect that in similar way shifted Kihara systems of variable range, modifying the exponents 12-6, could be also relevant in order to describe liquid crystalline phases.

We finally stress that the long-time relaxation dynamics of colloidal LCs has interesting common features with that of molecular (or thermotropic) LCs. The interested reader is referred to the experiments by Fayer and coworkers to gain an insight into the impact of randomization of pseudomorphic domains on the long-time relaxation and orientational dynamics of molecular LCs, especially observed close to the isotropic-to-nematic phase transition [48–50]. By contrast, at short time scales, the ballistic regime generally reported in molecular fluids, with \( \Delta r^2 \propto t^2 \), is never observed in colloidal suspensions, where Brownian motion dominates and determines the short-time diffusive regime, with \( \Delta r^2 \propto t \) as reported in Fig. 4 for both N and Sm phases.

V. ACKNOWLEDGMENTS

D.C. acknowledges support from CONACYT for funding her PhD scholarship. A.P. acknowledges financial support from the Leverhulme Trust Research Project Grant No. RPG-2018-415 and the Newton Mobility Grant NMG\textbackslash{}R2\textbackslash{}170137 awarded by The Royal Society to fund his visit at the University of Guanajuato in León.

[1] S. Sacanna, D. J. Pine, and G.-R. Yi, Soft Matter 9, 8096 (2013).
[2] L. Huber, R. Suzuki, T. Krüger, E. Frey, and A. R. Bausch, Science 361, 255 (2018).
[3] S. Fraden, G. Maret, D. L. D. Caspar, and R. B. Meyer, Phys. Rev. Lett. 63, 2068 (1989).
[4] Z. Dogic and S. Fraden, Current Opinion in Colloid & Interface Science 11, 47 (2006).
[5] E. Pouget, E. Grelet, and M. P. Lettinga, Phys. Rev. E 84, 041704 (2011).
[6] S. Sacanna, M. Korpics, K. Rodríguez, L. Colón-Meléndez, S.-H. Kim, D. J. Pine, and G.-R. Yi, Nat. Commun. 4, 1688 (2013).
[7] R. P. Murphy, H. W. Hatch, A. Mahynski, Nathan, V. K. Shen, and N. J. Wagner, Soft Matter 16, 1279 (2020).
[8] D. Frenkel, J. Phys. Chem. 92, 3280 (1988).
[9] S. C. McGrother, D. C. Williamson, and G. Jackson, J. Chem. Phys. 104, 6755 (1996).
[10] S. C. McGrother, A. Gil-Villegas, and G. Jackson, Mol. Phys. 95, 657 (1998).
[11] J. S. van Duijneveldt, A. Gil-Villegas, G. Jackson, and M. P. Allen, J. Chem. Phys. 112, 9092 (2000).
[12] M. P. Allen, Mol. Phys. 117, 2391 (2019).
[13] F. J. Guevara-Rodríguez and M. Medina-Noyola, Phys. Rev. E 68, 011405 (2003).
[14] P. Ramírez-González, L. López-Flores, H. Acuña Campa, and M. Medina-Noyola, Phys. Rev. Lett. 107, 155701 (2011).
[15] J. Jover, A. J. Haslam, A. Galindo, G. Jackson, and E. A. Müller, J. Chem. Phys. 137, 144505 (2012).
[16] I. M. Zerón, C. Vega, and A. L. Benavides, Mol. Phys. 116, 3555 (2018).
[17] C. A. Báez, A. Torres-Carbajal, R. Castañeda Priego, A. Villada-Balbuena, J. M. Méndez-Alcaraz, and S. Herrera-Velarde, J. Chem. Phys. 149, 164907 (2018).
[18] A. L. Davies, A. Gil-Villegas, and G. Jackson, Int. J. Thermophys. 19, 675 (1998).
[19] T. Lafitte, A. Apostolakou, C. Avendaño, A. Galindo, C. S. Adjiman, E. A. Muller, and G. Jackson, J. Chem. Phys. 139, 154504 (2013).
[20] S. Dufal, T. Lafitte, A. Galindo, G. Jackson, and A. J. Haslam, AlChe J 61, 2891 (2015).
[21] A. W. Metropolis, N. and Rosenbluth, M. N. Rosenbluth, A. H. Teller, and E. Teller, J. Chem. Phys. 21, 1087 (1953).
[22] E. Sanz and D. Marenduzzo, The Journal of Chemical Physics 132, 194102 (2010), https://doi.org/10.1063/1.3414827.
[23] F. Romano, C. De Michele, D. Marenduzzo, and E. Sanz, The Journal of Chemical Physics 135, 124106 (2011), https://doi.org/10.1063/1.3629452.
[24] A. Patti and A. Cuetos, Phys. Rev. E 86, 011403 (2012).
[25] A. Cuetos and A. Patti, Phys. Rev. E 92, 022302 (2015).
[26] D. Corbett, A. Cuetos, M. Dennison, and A. Patti, Phys. Chem. Chem. Phys. 20, 15118 (2018).
[27] M. Chiappini, A. Patti, and M. Dijkstra, Phys. Rev. E 102, 040601 (2020).
[28] F. A. García Daza, A. Cuetos, and A. Patti, Phys. Rev. E 102, 013302 (2020).
[29] F. A. García Daza, A. M. Puertas, A. Cuetos, and A. Patti, Journal of Colloid and Interface Science 605, 182 (2022).
[30] A. Cuetos, B. Martínez-Haya, S. Lago, and L. F. Rull, J. Phys. Chem. B 109, 13729 (2005).
[31] A. Cuetos and B. Martínez-Haya, Mol. Phys. 113, 1137 (2015), https://doi.org/10.1080/00268976.2014.996191.
[32] A. Cuetos, B. Martínez-Haya, L. F. Rull, and S. Lago, J. Chem. Phys. 117, 2934 (2002).
[33] C. Vega and S. Lago, Computers & Chemistry 18, 55 (1994).
[34] J. Bonet Avalos, J. M. Rubí, D. Bedeaux, and G. van der Zwan, Physica A 211, 193 (1994).
[35] N. Morillo, A. Patti, and A. Cuetos, The Journal of Chemical Physics 150, 204905 (2019).
[36] M. P. Lettinga, E. Barry, and Z. Dogic, EPL (Europhysics Letters) 71, 692 (2005).
[37] M. Cifelli, G. Cinacchi, and L. De Gae
tani, J. Chem. Phys. 125, 164912 (2006), https://doi.org/10.1063/1.2359428.
[38] R. van Roij, P. Bolhuis, B. Mulder, and D. Frenkel, Phys. Rev. E 52, R1277 (1995).
[39] J. S. Duijneveldt and M. P. Allen, Molecular Physics 90, 243 (1997), https://doi.org/10.1080/002689797172723.
[40] M. P. Lettinga and E. Grelet, Phys. Rev. Lett. 99, 197802 (2007).
[41] M. Bier, R. van Roij, M. Dijkstra, and P. van der Schoot, Phys. Rev. Lett. 101, 215901 (2008).
[42] A. Patti, D. El Masri, R. van Roij, and M. Dijkstra, Phys. Rev. Lett. 103, 248304 (2009).
[43] A. Patti, D. El Masri, R. van Roij, and M. Dijkstra, The Journal of Chemical Physics 132, 224907 (2010), https://doi.org/10.1063/1.3432864.
[44] G. Brambilla, D. El Masri, M. Pierno, L. Berthier, L. Cipelletti, G. Petekidis, and A. B. Schofield, Phys. Rev. Lett. 102, 085703 (2009).
[45] R. Matena, M. Dijkstra, and A. Patti, Phys. Rev. E 81, 021704 (2010).
[46] S. Belli, A. Patti, R. van Roij, and M. Dijkstra, The Journal of Chemical Physics 133, 154514 (2010), https://doi.org/10.1063/1.3505150.
[47] J. M. Falcón, C. Contreras-Aburto, M. Lara Peña, M. Heinen, C. Avendaño, A. Gil-Villegas, and R. Casta
tañeda Priego, J. Chem. Phys. 153, 234901 (2020).
[48] H. Cang, J. Li, V. N. Novikov, and M. D. Fayer, J. Chem. Phys. 119, 10421 (2003).
[49] J. Li, I. Wang, and M. D. Fayer, J. Phys. Chem. B 109, 6514 (2005).
[50] K. P. Sokolowsky, H. E. Bailey, and M. D. Fayer, J. Phys. Chem. B 118, 7856 (2014).