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Dynamical states in driven colloidal liquid crystals

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We study a model colloidal liquid crystal consisting of hard spherocylinders under the influence of an external aligning potential by Langevin dynamics simulation. The external field that rotates in a plane acts on the orientation of the individual particles and induces a variety of collective nonequilibrium states. We characterize these states by the time-resolved orientational distribution of the particles and explain their origin using the single particle behavior. By varying the external driving frequency and the packing fraction of the spherocylinders we construct the dynamical state diagram. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4901423>]

I. INTRODUCTION

The manipulation of liquid crystals by external fields is a key mechanism in electro-optical applications.¹ Therefore, it is not surprising that this has inspired a lot of research, both experimentally and theoretically. In this work we investigate the dynamical states that evolve in a colloidal liquid crystal under the influence of a rotating aligning potential. The advantage of colloidal over molecular systems lies in the fact that they can be directly studied in real space giving access to the dynamics of individual particles, e.g., Refs. 2 and 3.

There have been a number of studies on the field-induced behavior of isolated anisotropic colloidal particles, such as optically torqued nanorods,⁴ the electrorotation of nanowires,⁵ and magnetic rods in precessing magnetic fields.^{6–8} These studies agree that for low frequencies the particle dynamics show a linear regime in which the orientations of the particles simply follow the external field. For higher frequencies, however, the dynamics become nonlinear showing, for example, a periodic switching in rotation direction.^{4,7} In colloidal many-particle systems, the collective behavior depends critically on the shape of the particles and the type of time-dependent external field. For example, spheres with a permanent dipole assemble into layers under a rotating magnetic field.^{9,10} In systems of platelets between two flat parallel walls, rotating magnetic fields have been experimentally shown to induce a bend-splay Frederiks transition with transient spatially periodic patterns.¹¹ For rod-like particles, a linearly oscillating electric field will lead to a number of complex states and phases consisting of isotropic, nematic, and chiral nematic domains.¹²

We study the arguably most simple model system for a liquid crystal. Here the colloidal particles are represented by hard spherocylinders of aspect ratio $L/D = 5$ (see Fig. 1). In equilibrium¹³ this system exhibits several bulk phases depending on the packing fraction. The system is isotropic for low packing fractions. At a density of $\rho_{IN}^* \simeq 0.45$, the system undergoes a phase transition to a nematic state, where the particle orientations $\hat{e}$ show a preferred direction of alignment.

The dimensionless density ρ^* is throughout this work defined as the number density ρ , normalized to the density in the close packing limit $\rho_{cp} = (2D^{-3})/(\sqrt{2} + \frac{L}{D}\sqrt{3})$: $\rho^* = \rho/\rho_{cp}$. For even higher packing fractions, the system exhibits a smectic A phase, where layering of the particles occurs perpendicular to the preferred particle orientation. The corresponding nematic and smectic coexistence densities were found to be $\rho^* \simeq 0.513$ and $\rho^* \simeq 0.546$, respectively. Finally, for the highest packing fractions the system crystallizes in a hexagonal ABC solid with $\rho^* \simeq 0.669$ and $\rho^* \simeq 0.699$ the respective smectic and solid coexistence densities. All those phase transitions are purely driven by entropy since the system gains translational entropy by increasing the orientational order.

The packing fractions of the systems we study were chosen in the range where the equilibrium bulk system would be in an isotropic or nematic state. To investigate the influence of an external potential on such a system, the particles are subjected to an aligning field that rotates in a plane, as proposed by Härtel *et al.*¹⁴ In their dynamical fundamental measure density-functional theory study they observed a variety of dynamical states, depending on the packing fraction and driving frequency of the field. In light of recently discovered shortcomings¹⁵ of dynamical density functional theory (DDFT), it is worthwhile to revisit this system with computer simulations. Any observed deviations from DDFT would then also lend further support to recently proposed improvements of the theory.^{16,17} In addition, our Langevin dynamics simulations allow us to access the single-particle behavior, which is not possible in (dynamical) density functional theory. We are thus able to give a conclusive analysis of the origin and the underlying mechanisms of the different states.

The paper is structured as follows: In Sec. II we give the details of the simulation method and the system setup. The external potential is discussed in Sec. III, the results we obtain are presented in Sec. IV and we summarize our conclusions in Sec. V.

II. SIMULATION METHOD

In this work we model the colloidal system via a Langevin dynamics simulation where the solvent is not

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FIG. 1. Sketch of a spherocylinder with aspect ratio $L/D = 5$ in the equatorial plane. Its orientation is given by the normalized orientation vector $\hat{e}$; $\hat{u}_0$ indicates the alignment direction in which the external potential is minimal.

explicitly included. The equations of motion for translation and rotation can be written as¹⁸

$$\frac{d\vec{p}}{dt} = -\Xi \vec{v} + \vec{F}_S + \vec{F}_R, \quad (1)$$

$$\frac{d\vec{L}}{dt} = -\gamma_r \vec{\omega} + \vec{T}_S + \vec{T}_R, \quad (2)$$

where $\vec{p} = m\vec{v}$ and $\vec{L} = \mathbf{I}\vec{\omega}$ are the momentum and angular momentum of a particle with mass m and inertia tensor $\mathbf{I}$ with $\vec{v}$ and $\vec{\omega}$ its translational and angular velocity.

The first term on the right-hand side of Eqs. (1) and (2) accounts for viscous dissipation. The translational friction tensor Ξ depends on the translational friction coefficients $\gamma_{\parallel}$ and $\gamma_{\perp}$ for motion parallel and perpendicular to the symmetry axis $\hat{e}$ of particle i :

$$\Xi_i = \gamma_{\parallel} \hat{e}_i \otimes \hat{e}_i + \gamma_{\perp} (\mathbb{1} - \hat{e}_i \otimes \hat{e}_i). \quad (3)$$

The translational friction coefficients and the rotational friction coefficient γ_r are linked to translational and rotational diffusion via the Einstein-Smoluchowski relation $\gamma_i = k_B T / D_i$ with k_B as Boltzmann's constant, T the Temperature and D_i the respective diffusion constant. They only depend on size and aspect ratio of the particle and the viscosity of the fluid.¹⁹

The subscripts R and S in Eqs. (1) and (2) indicate the systematic and random contribution to the force $\vec{F}$ and torque $\vec{T}$, respectively. The random contributions are related to the friction according to the fluctuation dissipation theorem for particles i and j :

$$\langle \vec{F}_{R,i}(t) \rangle = \langle \vec{T}_{R,i}(t) \rangle = \vec{0}, \quad (4)$$

$$\langle \vec{F}_{R,i}(t) \vec{F}_{R,j}(t') \rangle = 2k_B T \Xi_i \delta_{ij} \delta(t - t'), \quad (5)$$

$$\langle \vec{T}_{R,i}(t) \vec{T}_{R,j}(t') \rangle = 2k_B T \gamma_r (\mathbb{1} - \hat{e}_i \otimes \hat{e}_i) \delta_{ij} \delta(t - t'), \quad (6)$$

$$\langle \vec{F}_{R,i}(t) \vec{T}_{R,j}(t') \rangle = \vec{0}, \quad (7)$$

with $\delta(t - t')$ the Dirac delta distribution, which in the case of discrete time steps of size Δt is replaced by $\delta_{tt'}/\Delta t$. For reasons of symmetry we keep $\vec{\omega}$ perpendicular to the symmetry axis of the spherocylinder given by the normalized orientation vector $\hat{e}$ (see Fig. 1). We therefore only apply random torques $\vec{T}_R$ perpendicular to this axis.

The systematic contributions originate from both the torque exerted by the external potential (see Sec. III) and

the particle particle interactions which in our model only arise from excluded volume, i.e., electrostatic interactions between colloids are neglected as they are assumed to be sufficiently screened by the ions in the solvent. We use the *pe* rigid body dynamics framework,^{20,21} with which we have already successfully studied hard-spherocylinder liquid crystals in equilibrium,²² to obtain the motion of the spherocylinders according to Eqs. (1) and (2) and to resolve collisions between particles. As the friction coefficients are not known analytically, we performed drag tests on the spherocylinders in a Lattice Boltzmann simulation and found them to agree quite well with the values given by Tirado *et al.*¹⁹ for cylinders with an aspect ratio of 5.7 at the same diameter. This can be understood by the fact that, while the cylindrical part of the spherocylinders has an aspect ratio of five, their total aspect ratio including the end caps is six.

The hard spherocylinder systems we evaluate in this work consist of between $N = 2304$ and $N = 9126$ particles at different densities ρ^* . Ongoing research also includes the influence of hydrodynamic interactions by coupling the particles to a Lattice Boltzmann simulation where inertia is inherent in the simulation algorithm. For reasons of comparability we therefore chose not simply to neglect the inertial terms, i.e., the left-hand side of Eqs. (1) and (2), in the present study. However, the particle mass and inertia were chosen such that the timescales $\tau_{ac_t} = m/\gamma_t$ and $\tau_{ac_r} = I_{\perp}/\gamma_r$ on which the translational and angular velocity autocorrelations decay are much smaller than the corresponding Brownian timescales τ_b . Here γ_t signifies the translational friction coefficient for motion in a random direction given by $[2/3\gamma_{\perp} + 1/3\gamma_{\parallel}]^{-1}$ according to Ref. 19 and $I_{\perp}$ is the moment of inertia perpendicular to $\hat{e}$. If we define the Brownian timescales as $\tau_{b_t} = L^2\gamma_t/6k_B T$ and $\tau_{b_r} = (\pi/2)^2\gamma_r/4k_B T$ we obtain ratios of $\tau_{ac_t}/\tau_{b_t} = 1.8 \times 10^{-4}$ and $\tau_{ac_r}/\tau_{b_r} = 1.0 \times 10^{-4}$. This difference in timescales is chosen to reduce the impact of inertia on our results. Furthermore, we use periodic boundary conditions in our simulations to minimize finite size effects.

III. EXTERNAL POTENTIAL

We investigate the dynamical states that evolve in the model liquid crystal under the influence of the external potential

$$V_{ext}(t, \hat{e}) = -V_0 (\hat{e} \cdot \hat{u}_0(t))^2 = -V_0 \cos^2(\omega_0 t - \varphi) \sin^2(\vartheta). \quad (8)$$

This potential acts on the orientation $\hat{e}$ of each individual particle, where φ and ϑ are its azimuthal and polar angle in spherical coordinates. It favors an alignment of the symmetry axis of the spherocylinder $\hat{e}$ to a direction $\hat{u}_0(t) = \pm(\cos \omega_0 t, \sin \omega_0 t, 0) = \pm(\cos \varphi_0, \sin \varphi_0, 0)$ that rotates in the xy -plane with a given frequency ω_0 . The $\pm$ originates from the symmetry of the particles that makes $\hat{e}$ equivalent to $-\hat{e}$ (see Fig. 1). In experiments, this could be realized by a high frequency electric field oriented along $\hat{u}_0(t)$ that induces dipole moments in the colloid particles.⁵ However, the resulting dipole-dipole interactions are absent in our simulation.

Throughout this work we keep the strength of the potential fixed at $V_0 = 5 k_B T$ and vary the rotation frequency ω_0 .

A. Single particle dynamics

Assuming an isolated spherocylinder aligned to the equatorial plane in the absence of noise, the torque exerted on it depends on the phase $\Delta\varphi = \omega_0 t - \varphi$ between the most favorable alignment direction $\hat{u}_0$ and the orientation of the particle $\hat{e}$ (see Fig. 1) as

$$\vec{T}_{ext} = V_0 \sin(2\Delta\varphi) \hat{e}_z. \quad (9)$$

In the steady state, the torque balance between this external torque $\vec{T}_{ext}$ and the rotational friction torque $-\gamma_r \vec{\omega}$ gives rise to a critical frequency of the external potential $\omega_0^* = V_0/\gamma_r$. Up to this frequency the particle orientation $\hat{e}$ will rotate with the same frequency as the external potential and the phase $\Delta\varphi$ between them is constant at

$$\Delta\varphi = \frac{1}{2} \arcsin\left(\frac{\gamma_r}{V_0} \omega_0\right). \quad (10)$$

With increasing ω_0 this phase shift increases until for ω_0^* a phase shift of $\pi/4$ is reached at which the external torque is maximal. For frequencies above ω_0^* there exists no solution with a constant phase shift as the corresponding friction would exceed the maximum torque the external potential can exert. Instead $\Delta\varphi$ will increase continuously although it can of course always be mapped into the interval of $[-\pi/2, \pi/2[$ due to the symmetry of the particles. For $0 < \Delta\varphi < \pi/2$ the particles are subjected to a torque that turns them in the same direction as the field is turning while for $-\pi/2 < \Delta\varphi < 0$ the torque acts in the opposite direction leading to a periodic reversal of turning direction. Every second reversal of the turning direction the particle has acquired an additional phase shift with respect to the external potential of π . For a detailed discussion of the nonlinear differential equation of motion see Refs. 4 and 5. Throughout this paper we give all frequencies as multiples of the critical frequency ω_0^* .

For a single particle at finite temperature, i.e., including Brownian noise, we observe some deviations from the idealized behavior described above. In the case of $V_0 = 5 k_B T$ even for driving frequencies as low as $\omega_0 = 0.1 \omega_0^*$ the particle will not follow the external potential minimum perfectly but will occasionally acquire an additional phase shift of $\pm\pi$ within a very short timespan. This forward or backward flip, respectively, is almost always accompanied by a strong deviation of ϑ from the equilibrium value of $\vartheta = \pi/2$. With increasing driving frequency the number of forward flips decreases quickly while the number of backward flips increases. The latter now also occur at ϑ closer to $\pi/2$ as diffusion in φ in combination with the increase in the zero temperature limit phase shift (Eq. (10)) raises the probability that the particle obtains a phase shift of $\Delta\varphi > \pi/2$, such that it is attracted to the subsequent potential minimum. For ω_0 larger than about $0.7 \omega_0^*$ the particle acquires an additional phase shift of π , i.e., turns backwards to the subsequent potential minimum, on average at least once per cycle of the external potential. On the other hand, Brownian motion occasionally allows the particle to follow the external field for more than one cycle even for driving frequencies slightly larger than ω_0^* . In the multi-

particle system we expect the diffusion of the particle orientation along ϑ to be strongly suppressed due to confinement by neighboring particles. Thus the jumps in φ via ϑ close to $\vartheta = 0$ or $\vartheta = \pi$ should be mostly suppressed.

B. Limiting cases of the many-particle system

In the limiting case of infinite driving frequency $\omega_0 \rightarrow \infty$ the spherocylinders feel an effective time-averaged potential $-V_0 \sin^2(\vartheta)/2$. From density-functional theory studies^{14,23} we expect to find two distinct regimes in density separated by a paranematic to nematic phase transition. We characterize the system by the three-dimensional order tensor $\mathbf{Q}_{3D}$

$$Q_{3D_{\alpha\beta}} = \frac{1}{N} \left(\sum_i \frac{3}{2} \hat{e}_{i\alpha} \hat{e}_{i\beta} \right) - \frac{1}{2} \delta_{\alpha\beta}, \quad \alpha, \beta = x, y, z. \quad (11)$$

The eigenvalues λ_i of this tensor are given in Fig. 2(a) sorted by $\lambda_1 \geq \lambda_2 \geq \lambda_3$ for different particle densities ρ^* . In the paranematic phase, they have the relation $\lambda_1 = \lambda_2 = -\lambda_3/2$. For a perfect paranematic alignment where all particle orientations $\hat{e}_i$ lie isotropically in one plane this would correspond to $\lambda_1 = \lambda_2 = 0.25$ and $\lambda_3 = -0.5$. For an uniaxial nematic phase the eigenvalues are related by $\lambda_1 = S$ and $\lambda_2 = \lambda_3 = -S/2$ where the largest eigenvalue S is the order parameter that gives the degree of nematic ordering, $S = 0$ corresponding to an isotropic state, $S = 1$ corresponding to perfect alignment of all particles. For a biaxial nematic state the eigenvalues of $\mathbf{Q}_{3D}$ are $\lambda_1 = S$, $\lambda_2 = -S/2 + T$, and $\lambda_3 = -S/2 - T$ where T is a measure of the biaxiality. In Fig. 2(a) one can clearly see the transition from a paranematic state at low densities ρ^* to a biaxial nematic state at higher densities that evolves towards an uniaxial nematic state with increasing density.

To demonstrate that the plane of isotropic distributions in the paranematic states coincides with the plane $\vartheta = \pi/2$ we also give the two-dimensional order parameter S_{2D} defined as the larger eigenvalue of the two-dimensional ordering tensor with respect to the x - y plane

$$Q_{2D_{\alpha\beta}} = \frac{1}{N} \left(\sum_i \frac{2}{\hat{e}_{ix}^2 + \hat{e}_{iy}^2} \hat{e}_{i\alpha} \hat{e}_{i\beta} \right) - \delta_{\alpha\beta}, \quad \alpha, \beta = x, y \quad (12)$$

FIG. 2. Eigenvalues λ_i of the three-dimensional order tensor $\mathbf{Q}_{3D}$ (a) and two-dimensional order parameter S_{2D} (b) over dimensionless density ρ^* .

(see Fig. 2(b)). A value of $S_{2D} = 0$ is characteristic for a system that is isotropic in φ , while $S_{2D} = 1$ indicates a system where all particles are aligned along the same azimuthal angle.

Our simulations thus confirm the phase transition reported in Ref. 14 for this system. We estimate the transition to occur at a dimensionless density of about $\rho_c^* = 0.39$ (Fig. 2). This value is slightly larger than the one given in Ref. 14. For densities lower than ρ_c^* the system exhibits a paranematic phase where the orientational distribution of the particles is isotropic in φ but peaked strongly around $\vartheta = \pi/2$. For densities above ρ_c^* an additional ordering arises in φ leading to a biaxial nematic phase with the director, i.e., the preferred direction of alignment, lying in the equatorial plane. The biaxiality arises from the fact that the orientational distribution of the particles is confined relative to the director along φ only by the entropy gain depending on the packing fraction while along ϑ an additional confinement due to the external potential is present. With increasing packing fraction the former effect becomes more and more dominant and therefore drives the system towards an uniaxial nematic state.

In the opposite limit of vanishing driving frequency $\omega_0 = 0$ the external potential induces a nematic state with the director aligned to the x -axis for all densities.

IV. RESULTS

To sample the space of dynamical states that evolve in the system under the influence of the external potential described in Sec. III, we either varied the driving frequency ω_0 at fixed density ρ^* or changed ρ^* at constant ω_0 . In the first case the systems were first equilibrated in the absence of an external potential. After equilibrium was reached, the external potential was switched on and the system was again allowed to equilibrate until a dynamical steady state evolved. In the second case a system with a fully developed dynamical steady state at $\rho^* = 0.48$ and $\omega_0 = 0.8\omega_0^*$ was used as initial configuration. The density was then successively lowered by rescaling the particle positions. For each new packing fraction the system again was allowed to relax to the corresponding dynamical state. Once the steady state had developed, we found no sign that the system's behavior depends on the preparation protocol.

In the following we will describe the dynamical states we found in detail. We focus on the angular distribution of the particle orientation vectors $\hat{e}$ and on the height I_p and orientation (φ_p, ϑ_p) of the peak with the highest intensity of this distribution. For a nematic phase this height would be closely linked to the order parameter, while the orientation would correspond to the nematic director, i.e., the largest eigenvalue of $\mathbf{Q}_{3D}$ (Eq. (11)) and the corresponding eigenvector, respectively. The reason we use I_p and (φ_p, ϑ_p) instead of the order parameter and the director, commonly used to characterize nematic liquid crystals, is that the latter are insensitive towards multiple peaks in the angular distribution, i.e., for two peaks of the same height the director would be aligned between them and even if the individual peaks are sharply defined the order parameter would have a low value as it gives the order with respect to the director. This would make it impossible for us

to discriminate between the breathing and the splitting state as well as between the overtaking and the unsplit and overtaking state (see below).

As the time independent part of the external potential $V_{ext}(\vartheta) = -V_0 \sin^2(\vartheta)$ ensures that the orientation of the peak lies in the equatorial plane, i.e., $\vartheta_p = \pi/2$, we can reduce this evaluation to tracking the azimuthal angle φ_p of the peak orientation. Furthermore, we average the angular distribution over the two representatives $\hat{e}$ and $-\hat{e}$ of the particle orientation. Thus the distribution is periodic in φ with a periodicity of π .

Movies of the time evolution of the azimuthal angular distribution for the different dynamical states are also available in the supplementary material.²⁴

A. High density regime ($\rho^* > \rho_c^*$)

For systems at high densities we discover a broad variety of dynamical states as depicted in Fig. 3.

1. Towing

At low frequencies (Fig. 3(a)), the individual particles are able to rotate at the same frequency as the external field. For the angular distribution this results in a nematic peak with constant intensity I_p . However, the phase difference $\Delta\varphi_p = \varphi_0 - \varphi_p$ is larger in the many-particle system than the phase shift expected for an isolated particle according to Eq. (10), since particle-particle interactions provide an additional source of friction. As the peak is dragged behind $\hat{u}_0$ at a constant phase shift $\Delta\varphi_p$, this state is called towing.¹⁴

2. Breathing

Upon increasing the driving frequency Brownian motion and particle-particle interactions, that hinder the particles in their turning, make it impossible for some particles to follow the external potential. As they get left behind, the intensity I_p of the peak decreases and $\Delta\varphi_p$ increases slightly (see Fig. 3(b)). If $\Delta\varphi$ of the stray particles becomes larger than $\pi/2$ they are attracted to the subsequent potential minimum and change their turning direction. When they are overtaken by the potential minimum at $\varphi_0 - \pi$ they again reverse their rotation direction and are collected into the peak at $\varphi_p - \pi$. As this peak is equivalent to the one at φ_p , as mentioned above, this leads to a re-increase in I_p and a decrease in $\Delta\varphi_p$. Due to this periodic change in I_p and $\Delta\varphi_p$ this state is called breathing. For the breathing frequency ω_b we find $\omega_b/\omega_0 > 1$ with a trend to higher ratios with increasing driving frequency. A proper quantitative analysis was not feasible due to noise and limited simulation time, however, the observed trend for the dynamical breathing state as well as the other states described below agrees rather well with the one observed by Härtel *et al.*¹⁴ in their density functional theory study. There they observed the frequency of peak intensity oscillations for $\rho^* = 0.5$ at the onset of breathing at about $1.34\omega_0$. With increasing driving frequency the ratio ω_b/ω_0 increases continuously through all observed dynamical states and converges towards two. The characteristic frequency of peak intensity oscillations arises from the timescale defined by the fraction

FIG. 3. Dynamical states evolving at $\rho^* = 0.48$. (Left) Snapshot of the angular distribution of the particle orientations taken at the time indicated by the arrow in the right figure. The color scale is normalized to the total number of particles. The cross marks the orientation of the potential minimum $\hat{u}_0(t)$, the arrow the turning direction. (Right) Azimuthal angle φ_0 of the potential minimum (dashed line) and of the maximum peak in the angular distribution φ_p (black dots) as well as the height I_p of this peak (gray line) over one period of the external potential. (a) Towing ($\omega_0 = 0.15 \omega_0^*$), (b) breathing ($\omega_0 = 0.34 \omega_0^*$), (c) splitting ($\omega_0 = 0.46 \omega_0^*$), (d) overtaking ($\omega_0 = 0.60 \omega_0^*$), (e) unsplit and overtaking ($\omega_0 = 0.68 \omega_0^*$).

of the external cycle for which the particles are still able to follow the field in combination with the time they turn against the field until they are overtaken by the subsequent potential minimum. In the limit of particles not following the field at all, the potential minimum would be aligned with the particles twice per cycle of the external potential thus giving rise to an internal breathing frequency of $2\omega_0$, albeit with an intensity oscillation amplitude of zero. This is the limiting case for the unsplit and overtaking state for $\omega_0 \rightarrow \infty$ (see below).

3. Splitting

With further increase in the external rotation frequency (Fig. 3(c)) the spherocylinders have less and less time to rear-

range amongst each other. Thus their orientations lag further and further behind $\hat{u}_0$ and with them the peak orientation φ_p . If ω_0 surpasses a certain value, $\Delta\varphi_p$ becomes larger than $\pi/4$. Thus the torque on the majority of the particles starts to decrease (see Eq. (9)) which leads to an even faster increase in $\Delta\varphi_p$. At the same time those particles that broke away from the main peak first are overtaken by the potential minimum at $\varphi_0 - \pi$ like in the breathing case. The torque on them increases until at some phase shift $\Delta\varphi \in]\pi, \pi + \pi/4[$, which is equivalent to a phase shift of $\Delta\varphi \in]0, \pi/4[$, they experience a stronger torque than those particles constituting the original peak at its current $\Delta\varphi_p \in]\pi/4, \pi/2[$. Thus they become no longer integrated into the main peak, but instead give rise to the formation of a second peak while the original peak continues to drop in intensity. As we track the orientation of the peak with the highest intensity, we see a discontinuity in φ_p when the newly formed peak surpasses the old one in intensity. This state is called splitting due to the fact that there is no longer only one peak on each hemisphere but two.

4. Overtaking

For even higher frequencies the modulus of the jump in azimuthal angle from the decaying peak to the one originating from particles left behind becomes smaller than $\pi/2$ (Fig. 3(d)). The reason for this is that with increasing ω_0 the phase shift $\Delta\varphi_p$ increases faster while at the same time particles that lag even further behind no longer have time to reorient very far before they are dragged again by the potential minimum at $\varphi_0 - \pi$. Following Ref. 14 the branches of φ_p in both Figs. 3(c) and 3(d) can each be combined to a unique function $\varphi_p(t)$ such that the modulus of the jumping angle is always smaller than $\pi/2$. This would make the splitting state correspond to a peak jumping forwards, while in the case of Fig. 3(d) the peak in the angular distribution is overtaken by the potential minimum once during each breathing cycle of I_p hence the name overtaking.

5. Unsplit and overtaking

Finally, above a certain frequency ω_0 , we again observe only one peak (Fig. 3(e)). Here the orientation of the majority of the particles falls rather quickly behind $\hat{u}_0$. As soon as $\Delta\varphi_p$ becomes larger than $\pi/4$ the aligning torque on the main part of the spherocylinders decreases leading to a broadening of the peak accompanied by a drop in intensity I_p . As in the cases above, particles that gain a $\Delta\varphi$ larger than $\pi/2$ are attracted to the minimum at $\varphi_0 - \pi$ and change their turning directions. But before they become fully separated from the main peak, $\Delta\varphi_p$ itself becomes larger than $\pi/2$. Thus the whole peak starts to turn in the opposite direction as the external potential. At the same time those particles with the largest $\Delta\varphi$, i.e., those that are overtaken by the potential minimum at $\varphi_0 - \pi$, again change their turning direction and are pushed back towards the peak leading to a re-increase in I_p . When the peak itself is overtaken by the potential minimum at $\varphi_0 - \pi$ it too reverses its turning direction. While the peak is dragged by the external potential it collects those particles with $\Delta\varphi < \Delta\varphi_p$ gaining further in intensity I_p until above

FIG. 4. Dynamical states at $\rho^* = 0.25$. Symbols as in Fig. 3. (a) Towing ($\omega_0 = 0.21 \omega_0^*$), (b) breathing ($\omega_0 = 0.80 \omega_0^*$), (c) towing II ($\omega_0 = 5.00 \omega_0^*$).

$\Delta\varphi_p = \pi + \pi/4$ the process repeats itself. As there is now only one peak that is periodically overtaken by the preferred direction of alignment this state is known as unsplit and overtaking. For further increase in the driving frequency ω_0 , we expect the amplitude of the peak oscillations to decrease continuously until in the case of $\omega_0 \rightarrow \infty$ a biaxial nematic state with constant peak height I_p evolves (see Sec. III B).

B. Low density regime ($\rho^* < \rho_c^*$)

In the low density regime we observe three dynamical states that are depicted in Fig. 4.

1. Towing

At low frequencies (Fig. 4(a)), we find again the behavior described above as towing. Here the difference between $\Delta\varphi_p$ and the phase shift in the isolated particle case is not as prominent as in the high particle density regime as particle-particle interactions are less dominant.

2. Breathing

For intermediate driving frequencies (Fig. 4(b)) the system develops a dynamical breathing state that corresponds qualitatively to the one observed for higher packing fractions. However, as the inter-particle interactions are less pronounced than at high particle densities the transition between towing and breathing occurs at higher driving frequencies than in the denser packed system. Additionally, this results in both a lower peak intensity and a lower breathing amplitude than in Fig. 3(b).

3. Towing II

At frequencies beyond the critical frequency the individual particles cannot follow $\hat{u}_0$. Their orientations are rather

FIG. 5. Dynamical state diagram over driving frequency of the external potential ω_0 in units of the critical frequency ω_0^* and reduced particle density ρ^* . Dashed lines serve as guide for the eye. ρ_c^* and ρ_{IN}^* give the densities of the paranematic-nematic phase transition in the limit of $\omega_0 \rightarrow \infty$ and the equilibrium isotropic-nematic transition, respectively. For description of the various states see text.

isotropically distributed in φ as the system is driven towards the paranematic state. The peak visible in Fig. 4(c) arises from those particles that have a $\Delta\varphi$ of close to $\pi/4$ towards the current orientation of $\hat{u}_0$ and thus feel a stronger torque than the other particles. They start to rotate with the external potential until friction becomes dominant, contributing for that time to a peak in the angular distribution that is following $\hat{u}_0$. This is a rather subtle effect as can be seen by the strong noise in $\Delta\varphi_p$ and the intensity scale of Fig. 4(c) in comparison to Fig. 4(a). We expect the peak intensity to continuously decrease further with increasing ω_0 until it vanishes for $\omega_0 \rightarrow \infty$ in the paranematic state (see Sec. III B). To discriminate this purely collective soliton-like phenomenon from the synchronized turning of individual particles we call it towing II.

C. Nonequilibrium state diagram

Our findings are summed up in the nonequilibrium state diagram depicted in Fig. 5. The dashed lines separating different states are a guide for the eye. The closer the system's parameters are to these boundaries the harder it is to classify its state unambiguously as it switches back and forth between neighboring states. We attribute this to the finite size of the system. The states given in Fig. 5 correspond to the predominant state for each point in ρ^* and ω_0 . If we compare the dynamical state diagram to the one calculated by dynamical fundamental measure density-functional theory by Härtel *et al.*,¹⁴ we find a very good qualitative agreement at high densities. There we observe the same states in identical order. However, for the low density regime we are able to discriminate between two distinct kinds of towing with a breathing transition regime between them where density-functional theory only observes towing. This is partly due to the fact that it is impossible to distinguish between single particle rotation (towing) and the rotation of the director based on soliton-like dynamics (towing II) in density-functional theory.

In a quantitative comparison, we find that the frequency band in which the different states emerge is considerably broader and lies at far lower frequencies than reported by

Härtel *et al.*¹⁴ Part of this discrepancy could be due to inertial effects as these have been reported to influence the boundaries between states.¹⁰ Clearly, in our Langevin dynamics simulation inertia plays a non-negligible role, although we tried to minimize it (see Sec. II), while in Ref. 14 the spherocylinders are assumed to perform a completely overdamped Brownian motion. On the other hand, Härtel *et al.*¹⁴ observe even for the high density systems that the towing regime extends to more than five times the critical frequency ω_0^* . This is in direct contrast to our findings that already below the critical frequency towing is not possible due to particle interactions. Even more so it is in disagreement with the single particle assessment (Sec. III A) according to which towing is prohibited for frequencies above the critical frequency. In dynamical density functional theory, the approximation is made that the two-particle distribution function in a non-equilibrium system is equal to the equilibrium one for the same density profile. In our system, particles collide more often with each other due to the time-dependent external torques than they would in a system with a time-independent external field. As a result, the positional dependence of the two-particle distribution function should change compared to the equilibrium result at the same density profile and the assumption made in DDFT cannot be expected to hold. Therefore, it is surprising that the DDFT does correctly predict which phases appear in this system.

V. CONCLUSIONS

We have simulated the behavior of a model colloidal liquid crystal consisting of hard spherocylinders under the influence of a periodic external potential that turns in a plane and acts on the orientation of the individual particles. We observe six different dynamical states that depend on the packing fraction of the particles and on the frequency of the external potential at fixed potential strength. These states have been categorized by the characteristic behavior of the angular distribution of the particle orientations as towing, towing II, breathing, splitting, overtaking, and unsplit and overtaking.

At high packing fractions we find the same states as density-functional theory.¹⁴ However, we observe a broad frequency range in which the dynamical states are found in contrast to the predictions of Ref. 14. Moreover, we are able to distinguish between two distinct types of towing with an intermediate breathing regime at low packing fractions, which have both not been reported by density-functional theory. The quantitative comparison leads us to the conclusion that with Langevin dynamics simulation we are able to provide a more reliable assessment of the state boundaries than given in previous studies.

We have analyzed the dynamical states we observe in detail and have given a thorough description from the single particle behavior point of view thereby explaining the underlying mechanisms that lead to the formation of those states. The towing behavior observed at low driving frequencies is a

state in which the rotation of each particle is synchronized with the external potential as observed for isolated particles.^{4,5,7} The dynamical states developing for higher frequencies originate from the interplay of the torque due to the external potential, friction with the fluid, Brownian motion and particle-particle interactions. Here individual particles exhibit a periodic reversal of their turning direction, also seen for isolated particles at high frequencies.^{4,7} The fraction of particles that turn against the field which increases with both driving frequency and packing fraction (i.e., particle-particle interactions) determines the individual state.

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- ²⁴See supplementary material at <http://dx.doi.org/10.1063/1.4901423> for movies of the time evolution of the azimuthal angular distribution of the particles for the different dynamical states.