Simulating tactoids of chiral rod-like particles

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We present simulations of rod-like particles that assemble into spindle-shaped droplets, so-called tactoids, in presence of depleting but non-self interacting (Asakura-Oosawa) spheres. The shape and structure of these objects depend on the density of the depletants and on the molecular parameters of the model rod-like particles. A special property of the simulated rods is their chirality that is induced by having a helical arrangement of point charges at the surface of the rods. An equilibrium bulk phase of such particles is a cholesteric liquid crystal phase. However, in the small assemblies studied in the present work, the formation of the cholesteric phase is suppressed.

1 Introduction

Systems of rod-like particles show a variety of equilibrium bulk phases (Gennes et al., 1995). Starting from an isotropic phase at low concentration (uniformly distributed positions and orientations) phase transitions to anisotropic (liquid crystalline) phases are found for increasing concentration. In the nematic phase the positions are still uniformly distributed, but the rods are oriented along a common direction (defined by the director). This phase actually is a special case of the cholesteric (or chiral nematic) phase, where the director rotates through space with some periodicity called the cholesteric pitch. For the nematic phase the cholesteric pitch is infinite. Increasing the concentration further leads to the transition to smectic phases, which are characterized by a one-dimensional layering. Within the layers

the positions are still uniformly distributed and the director may either coincide with the layer normal (Smectic-A) or be tilted to that (Smectic-C). For even larger concentrations the system shows solid phases. The cholesteric phase (which we are most interested in) occurs for example in systems of particles with chiral interactions (distinction between left- and right-handed). Many natural and synthetic molecules fall into this category; to name a few these, are cellulose nanocrystals (Lagerwall et al., 2014), *fd* virus (Grelet et al., 2003; Dogic et al., 2006), DNA (Livolant, 1991), chiral biphenyls (Solladié et al., 1996), or copolymers consisting of γ-benzyl glutamate and γ-alkyl glutamate (Watanabe et al., 1987).

Between (either in terms of the transition or indeed in space) bulk isotropic and bulk liquid crystalline phases the tactoids, (chiral) nematic droplets, are found (Wang et al., 2018; Park et al., 2014; Kim et al., 2013). Due to fluctuations in density, some parts of the system transit from isotropic to nematic phase, resulting in an interface between the phases. To have stable tactoids, the energy cost for this interface needs to be balanced by the free energy gain due to the formation of the (favoured) nematic phase. I. e. the tactoid only survives when its volume is large enough compared to its surface area. For spherical particles and the vapour-liquid transition, the tactoids (droplets) would be spherical to minimize the surface area for a given volume. For rod-like (elongated) particles there are two more effects: The particles prefer to have a uniform orientation and (usually) prefer to be in parallel alignment with the interface (planar anchoring). The competition of all effects determines the resulting shape (spindle-like or spheroidal) and structure (uniform, bipolar or twisted director field) of the tactoids.

The big goal would be to control the properties of liquid crystals starting from controlling the properties of the tactoids and their directed coalescence (without topological defects). Especially cholesteric liquid crystals are useful for optical applications, like displays or sensors (Dreher et al., 1973; Yeh et al., 2010; Saha et al., 2012; Picot et al., 2013). With our simulations we want to contribute to this goal by relating the microscopic (model) parameters and system conditions to the properties of the formed tactoids.

2 Theory

The above described competition of different effects is theoretically described by a free energy $F = F_E + F_S$, which is the sum of the Frank elastic energy F_E and a surface or interfacial free energy F_S. Shape and structure of the tactoids are adjusted to minimize this free energy. The Frank elastic energy is described by the volume integral (Virga, 1995; Prinsen et al., 2003; Prinsen et al., 2004a; Prinsen et al., 2004b):

$$F_E = \frac{1}{2} \int_V \mathrm{d}^3\mathbf{r} \left[K_{11} \left(\nabla \cdot \mathbf{n} \right)^2 + K_{22} \left(\mathbf{n} \cdot \nabla \times \mathbf{n} \right)^2 + K_{33} \left(\mathbf{n} \times \nabla \times \mathbf{n} \right)^2 \right] , \quad (1)$$

where the three terms correspond to splay, twist and bend deformation of the director field $\mathbf{n}(\mathbf{r})$, respectively. This part acts as a penalty for any deformation of the director field from being uniform ($\mathbf{n}(\mathbf{r}) = \mathbf{n}_0$), and the Frank elastic constants K_{11}, K_{22}, K_{33} determine the strength of this penalty for each kind of deformation. The interfacial free energy is described by the surface integral:

$$F_S = \tau \int_S \mathrm{d}^2\mathbf{r} \left(1 + \omega \left(\mathbf{q} \cdot \mathbf{n} \right)^2 \right) , \quad (2)$$

where τ is the interfacial tension, ω is the anchoring strength and $\mathbf{q}(\mathbf{r})$ defines the normal of the surface. The first term acts to minimize the surface of the tactoid and the second term acts as a penalty for non-planar alignment of the director to the surface. The strength of this penalty increases with interfacial tension and anchoring strength.

3 Simulations

To simulate droplets of an anisotropic phase surrounded by an isotropic phase, we use two species. One is a chiral rod-like particle and the other is a spherical particle acting as depletant to the rods. The rods are so-called helical Yukawa rods (Wensink et al., 2011; Honorato-Rios et al., 2016): The core is a hard spherocylinder of length L and diameter D and it is decorated with n^{pc} point charges in a helical

arrangement with internal pitch p^{int}, cf. Fig. 1. Those charges interact via a Yukawa potential:

$$U_{\text{Y}}(r) = k_{\text{B}}T \left(\frac{Z}{n^{\text{pc}}} \right)^2 \lambda_{\text{B}} \, \frac{\exp\left[-\kappa r\right]}{r} \, , \tag{3}$$

with r the distance between the point charges, Z the sum of the strength of the n^{pc} charges, λ_{B} the Bjerrum length, κ the Debye screening constant, k_{B} Boltzmann's constant, and T the temperature. The solvent is implicit and determines λ_{B} and κ. Using the elementary charge e, the permittivity of the solvent $\epsilon_0 \epsilon_{\text{r}}$, the number density of rods $\rho = N/V$ and the added salt concentration c_{s}, λ_{B} and κ are defined as:

$$\lambda_{\text{B}} = e^2/(4\pi\epsilon_0\epsilon_{\text{r}}k_{\text{B}}T) \tag{4}$$

$$\kappa = \sqrt{4\pi\lambda_{\text{B}}(Z\rho + 2c_{\text{s}})} \, . \tag{5}$$

Note, that counter ions and salt ions are not simulated explicitly, but act implicitly by determining the screening length κ^{-1}.
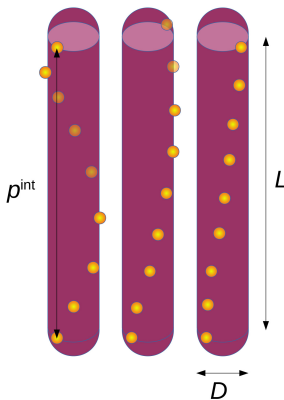
Figure 1: Sketch of helical Yukawa rods with length L, diameter D and different internal pitches (left $p^{int} = L$, middle $p^{int} = 2L$, right $p^{int} = 4L$), with the number of point charges $n^{\text{pc}} = 9$. Reprinted from Front. Mater. 3, 00021, 2016 (published under the terms of the Creative Commons Attribution License (CC BY)).

The total energy of a system is the sum of all Yukawa interactions between charges on different rods with distance $r < r_{\text{c}}$, where the cutoff distance r_{c} is between $2D$ and $4D$.

The spheres are so-called Asakura-Oosawa spheres (Asakura et al., 1954): They do not interact with each other, but they have a hard core of diameter $D_{ao} = 2D$ w. r. t. the rods. So they act as depletants to the rods leading to an effective attraction of the rods and therefore allowing for the formation of assemblies. There is no additional soft interaction between the spheres and the rods.

To find the equilibrium configuration of the systems, we apply Metropolis Monte Carlo simulations. I. e. we propose single particle moves (translation, rotation of the long axis or rotation around the long axis) of randomly chosen rods and accept the new configuration according to the Metropolis acceptance criterion: If the Boltzmann factor $\exp\left(-(E^{new} - E^{old})/k_B T\right)$ of the energy difference between old and new configuration is larger than a random number (uniformly drawn from $[0,1)$) the new configuration is accepted, otherwise it is rejected. Because of the hard core of the rods, overlaps between rods or rods and spheres are not allowed; thus, moves to overlapping configurations are rejected. The step sizes for the particle moves are adjusted to have an acceptance rate of 0.5.

At this point we are not interested in the nucleation process. Therefore, initial configurations already contain an assembly of rods. The number density of Asakura-Oosawa spheres needs to be large enough to keep the demixed state stable. The spheres are not stored as individual objects, but are inserted around the rods one at a time following the scheme described in (Glaser et al., 2015). This is called implicit depletant simulation and saves memory compared to the explicit simulation, in which the number of spheres would exceed several millions. The simulation box is chosen to be large enough to avoid interactions of rods across the periodic boundaries.

We use compute clusters to identify interesting regions of the parameter space by scanning through sets of parameters in parallel. The code itself is not highly parallelized: Neighbor lists are used for the energy calculation and two parallel threads share this task.

We measure density profiles, director fields and nematic order parameter profiles, and volume and aspect ratio of the tactoids. The nematic order parameters and

directors are determined locally. They are defined as the largest eigenvalue and the corresponding eigenvector of the order parameter tensor:

$$Q_{ij} = \frac{1}{N_L} \sum_{\alpha=1}^{N_L} \frac{3}{2} \left(u_\alpha^i u_\alpha^j - \frac{1}{3} \delta_{ij} \right) , \tag{6}$$

where u_α is a unit vector pointing along the long axis of rod α, $\{i,j\} = \{x,y,z\}$ its components and N_L the number of rods that are considered locally.

We vary the number of rods, the number of depletants and the chirality (no charge, different internal pitch).

4 Results

We study systems of $N = 500$ to $N \approx 4000$ rods of aspect ratio $L/D = 10$. The number density of Asakura-Oosawa spheres ranges from $\rho_s D^3 = 0.46$ to 1.8. A snapshot of a tactoid with $N = 2916$ and $\rho_s D^3 = 1.0$ is shown in Fig. 2.
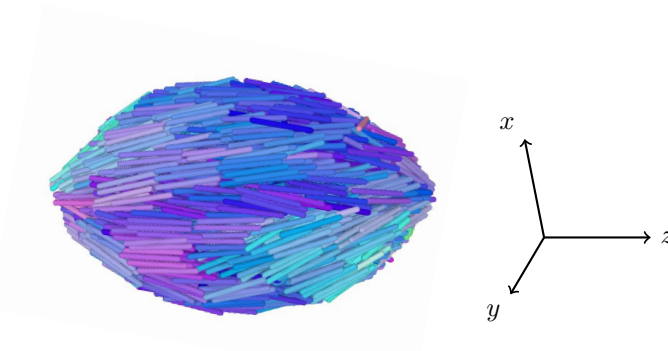
Figure 2: Snapshot of a tactoid with $N = 2916$ helical Yukawa rods with internal pitch $p^{\text{int}}/D = 20$ and depletant density $\rho_s D^3 = 1.0$. The Asakura-Oosawa spheres surrounding the tactoid are not shown. The z-axis of the co-ordinate system is chosen to coincide with the long axis of the tactoid.

4.1 Effect of tactoid volume

In an earlier simulation study using uncharged hard rods (Trukhina et al., 2009), it was found that small tactoids have a uniform director field, whereas larger ones have a bipolar director field; which is in accord with theoretical predictions (Prinsen

et al., 2003; Prinsen et al., 2004a; Prinsen et al., 2004b; Kaznacheev, Bogdanov and Taraskin, 2002; Kaznacheev, Bogdanov and Sonin, 2003). The reason is that surface free energy and elastic free energy scale differently with the size of the tactoid. For small tactoids the penalty to have non-planar alignment of the rods with the interface is smaller than that of deforming the uniform director field. For large tactoids it is much easier to pay for the deformation to a bipolar director field, this way reducing the interfacial energy by planar alignment. Thus, in the limit of infinite volume, the tactoids would be bipolar spheres.

Using the helical Yukawa rods instead, the qualitative behavior is similar, but there are two effects due to the repulsive chiral interaction between the rods: It is easier to deform the director field (the equilibrium phase is cholesteric, which is by definition non-uniform). And the anchoring strength is enhanced, because there is no electrostatic interaction between the rods and the Asakura-Oosawa spheres. So the assembly tries to expose as many charges as possible to the surface. Hence, also quite small tactoids show a less uniform director field compared to the hard rod equivalent.

4.2 Effect of chiral interaction

As discussed in the previous subsection, the repulsive chiral interaction increases the anchoring strength and eases the deformation of the director field. There are many parameters that influence the interaction, e. g. the ionic strength due to counter ions and added salt or the internal pitch of the charge helix. It is still difficult to predict the macroscopic equilibrium properties of a bulk cholesteric liquid crystal from the model parameters (or microscopic parameters of mesogens in general) and system conditions. We found that the internal pitch has a huge effect, especially on the alignment of rods (Kuhnhold and Schilling, 2016; Kuhnhold, Giesen et al., 2018) (large pitch enhances alignment, small pitch suppresses it). So we tested the effect of different internal pitches $p^{\text{int}}/D = 20$ or 40.

We show the director fields in cylindrical coordinates in Fig. 3 (z-axis as indicated in Fig. 2, and $\rho^2 = x^2 + y^2$). We assume cylindrical symmetry and average directors and nematic order parameters over the azimuthal angle φ. The color encodes the orientation of the director w. r. t. the ρ-z plane: red: parallel to the z-axis, blue/black: tilted within the plane, and green/magenta/turquoise: increasingly tilted out of the plane. A perfectly uniform tactoid would be red everywhere; a perfectly bipolar

tactoid would be red in the center and blue towards the surface; and a twisted tactoid would show different colors in a periodic fashion. The internal pitch in the left panel is $p^{\mathrm{int}}/D = 20$ and in the right panel it is 40. We observe a clear difference in the director field. The largest out-of-plane tilt (turquoise color) is found in Fig. 3b for the larger pitch. But for the smaller pitch (a and c) larger parts of the director fields are tilted out-of-plane (best seen by the magenta parts). However, for none of the cases studied so far we find a truly twisted director field; the reason for this being the rather small size of the tactoids.
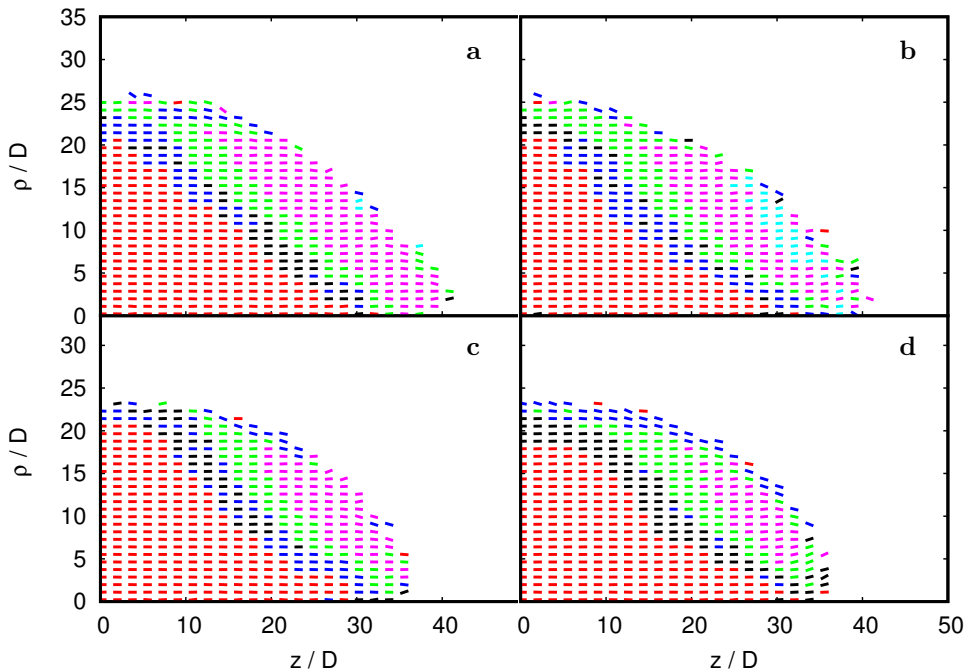
Figure 3: Director field of nematic tactoids for different internal pitch p^{int} and depletant density ρ_s shown in a cylindrical coordinate system ρ, z (symmetric in φ and for $z \to -z$). a: $p^{\mathrm{int}}/D = 20$, $\rho_s D^3 = 0.68$; b: $p^{\mathrm{int}}/D = 40$, $\rho_s D^3 = 0.68$; c: $p^{\mathrm{int}}/D = 20$, $\rho_s D^3 = 1.00$; d: $p^{\mathrm{int}}/D = 40$, $\rho_s D^3 = 1.00$. The bars represent local directors and the color supports the identification of the director orientation: red: parallel to long axis, blue/black: tilted within the ρ-z plane, green/magenta/turquoise: tilted out of the plane by increasing amount.

4.3 Effect of depletant density

The density of depletant Asakura-Oosawa spheres ρ_s has two effects. First, a higher density increases the effective attraction of the rods and therefore leads to smaller tactoid volumes, and second, the interfacial tension τ also increases with increasing ρ_s. In the top panel of Fig. 3 the depletant density is $\rho_s D^3 = 0.68$ and in the bottom panel it is 1.0. The larger density leads to more compact tactoids (smaller volume, higher concentration of rods within tactoid). Those tactoids show a much less fraction of out-of-plane tilt due to the denser packing. Due to the increased interfacial tension, those tactoids are closer to the perfect bipolar structure, which is indicated by the blue color at the tactoid surface.

5 Conclusion

We showed results of Monte Carlo simulations of chiral rod-like particles assembled to nematic droplets, so-called tactoids. The shape and structure of the tactoids is determined by the interplay between elastic and interfacial free energy, and also depends on the tactoid volume. Because of the chiral interaction, which leads to a cholesteric bulk phase, the formation of non-uniform tactoids is easier compared to assemblies of non-interacting rods. We observe a clear dependence of the director field on the internal pitch of the charge helix of our model mesogen. To properly interpret our results, more simulations with different model parameters are needed.

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