Simulating Liquid Crystals

Here I present an investigation into the phase behaviour of an exciting new DNA-based liquid crystal system. As well as having direct applications in a new generation of biological liquid crystal display technology, our understanding of the phase behaviour of DNA oligomers fuels the development of DNA nanostructure development.

# Introduction

I will briefly introduce the theoretical concepts key to this project, as well as outlining a few of the applications of DNA-based liquid crystal technology. My simulations were based on two systems; initially I considered a simple ‘rigid-rod’ system to benchmark and validate the simulation methods against known results. I then implemented the novel nunchuck system, and will present these results separately, demonstrating the existence of quasi-nematic phases in this system and illustrating the application of dynamic studies in phase detection.

**Liquid Crystals:** Liquid crystal is used as a broad term to encompass many materials with behaviours between that of conventional liquids and crystalline solids. This is easiest to characterise from a symmetry perspective; crystalline solids display translational and rotational symmetry (i.e. positional and orientational order) through the alignment of particles on a lattice, while liquids do not display any such order. Here we will focus on two particularly common phases, depicted in onscreen.

Firstly, we consider the nematic phase, which displays long range orientational order throughout the sample as all molecules are orientated along the same axis. We may also introduce positional order along one axis to form the smectic phase, leading to layers of similarly alignment molecules, as depicted in the centre of the figure here.

**Phase Transitions:** There are two primary classes of phase transition. Here we will focus solely on lyotropic phase transitions which are driven by changes in concentration, as opposed to temperature driven thermotropic transitions. Furthermore, we consider entropically driven phase transitions where the interaction potentials are purely repulsive. These are an effective benchmark for DNA-based systems; where Debye screening means the potential is almost purely repulsive.

**Order Parameter:** These phase transitions may be defined by an order parameter, which quantifies the degree of order in a given phase and is chosen such that it is non-zero in the ordered phase but vanishes in the isotropic phase.

For the nematic order parameter S\_n, we traditionally use the second Legendre polynomial of cos (theta), where theta is the angle between each molecule’s axis and the system director. Similarly, we introduce a smectic order parameter S\_s, to characterise the formation of one-dimensional positional order, by taking Fourier component of the normalised density along the director n, for layers or periodicity L.

**DNA:** It has long been known that even short DNA oligomers may form liquid crystalline structures at high concentrations, such as the one depicted onscreen. In fact it is ideal for this purpose, due to the high specificity with which it can be reliably manufactured and tuned on the nanoscale. We are particularly interested in phase structures formed by anisotropic particles, as these may be involved in the development of improved liquid crystal displays.

These techniques may also be applied to the development of DNA origami, where complex nano-structures are constructed out of DNA molecules. Though a greater understanding of the phase behaviour of DNA nanoparticles, we may inform design of more complex structures, and develop colloidal self-assembly processes. Applications of this are broad ranging, but one such example pictured on the right uses DNA origami to measure antibody binding affinities.

# Methods

I will now introduce the nunchuck molecules considered in this report, and outline the simulation methods used. In contrast to many earlier studies of anisotropic mesogen phase behaviour, which use a Monte Carlo approach, we utilise molecular dynamics simulations to explore the dynamic behaviour of the system as well as the static behaviour.

**Nunchuck Molecules:** We are considering ‘nunchuck’ molecules formed of two rigid rods connected by a flexible linker, as depicted on the left. These rods are formed of double stranded DNA (assumed to be completely rigid as they are shorter than the persistence length of DNA), connected by a linker of single stranded DNA. This linker allows the configuration to vary from fully stretched to folded.

However, as the interaction potential of such anisotropic particles is rather complex, we consider each molecule as a system of connected spheres, each with a separate isotropic interaction potential. This is depicted on the right, where the red spheres have adapted properties to allow for a flexible bond angle.

**Simulation Structure:** All molecular dynamics simulations were completed in LAMMPS, a medium coarse-grained, classical molecular dynamics code developed to replicate solid-state materials and soft matter mesoscopic systems. A soft-core particle model was used, with a shifted, cut-off Lennard-Jones potential representing the repulsive, pair-wise interactions between molecules. Here, sigma is the characteristic lengthscale, and epsilon the characteristic energy scale.

I typically consider a system of 1000 molecules, formed of 10-15 sequentially connected force-centres, and apply alternating stages of contraction/expansion (where the volume fraction is varied) and equilibration (where the volume is held constant, and equilibrium properties sampled).

# Rigid Rod Simulations

I initially consider the transition to the nematic phase (depicted on screen) in a test system of rigid, linear rods (where the opening angle is fixed at 180 degrees). This system is well studied, and we expect a phase transition at a volume fraction of 40% according to theoretical predictions made by Onsager.

**Nematic Phase Transition:** Here, the evolution of the volume fraction (in blue) and the nematic order parameter (in red) are plotted over the timescale of the simulation, for a system of 1000 rigid rods with aspect ratio 10. The phase transition is observed through a discrete change in the order parameter (in red), occurring after the volume fraction is increased above 0.4, as anticipated. This agreement with Onsager’s predictions was substantiated by further simulations of rods of extended aspect ratios, all giving nematic phase transitions within 5% of the theoretical value.

Note that the contraction steps (where volume fraction is changed) here are not of equal durations, and so do not correspond to equal changes in the system volume; rather they are chosen to highlight the phase transition. The timescale of contraction is much less that the timescale of equilibration, but the changes in volume fraction are not instantaneous, despite their appearance here.

**Smectic Phase Transition:** I also consider simulations initiated from a perfectly ordered crystalline phase region, to eliminate the possibility of hysteresis in the phase transition, and hence confirm this was a true equilibrium transition. A first order phase transition for the nematic to isotropic phase is observed in blue, again occurring after the volume fraction is decreased below 0.4, and hence validating the equilibrium nature of this transition.

Through the higher volume fractions achieved in this simulation method, I was also able to identify a continuous (second-order) phase transition from the smectic to the nematic phase, observed (in green) at high volume fractions. Note that there are multiple steps in the smectic order parameter, indicating this transition occurs over a range of volume fractions.

# Nunchuck Simulations

Further simulations applied the same approaches to the nunchuck molecules introduced in Section These could be configured in two ways; either with a fixed angle between the two rigid arms, or a fixed rigidity (which limits the distribution of angles observed).

Previous work by Jiaming Yu using OxDNA [54] has suggested that the fixed rigidity model provides an accurate coarse-grained model of the nunchucks; and so I initially considered particles with a variable opening angle, limited by the rigidity of the corresponding bond.

**Fixed Rigidity:** Here, we observe strong evidence for order formation through the formation of a favoured angle distribution throughout the sample, even in the limit of complete flexibility where there is no minimum opening angle. The figure shows the development of this peak in opening angle as the system evolves over time from the blue lines (where the angle distribution is uniform and so molecules were likely to have any opening angle) to the yellow lines (where there is a strong preference for large opening angles).

These large opening angles enable the formation of a quasi-nematic phase, as the rods are almost linear. This is an example of an entropically driven phase transition, as the system has sacrificed configurational entropy (by adopting a constant opening angle) in favour of translation entropy (as the nematic phase allows increased mobility along the system director), at high volume fractions.

**Fixed Angle:** To encourage the formation of non-traditional nematic phases, I therefore restricted the opening angle below 180 deg. It is also hoped that a uniform opening angle will also aid ordered phase formation, particularly if a regular angle conducive to repeating structures (such as 120 degrees) is chosen.

Simulations were conducted for opening angles of 90, 120 and 150 degrees, as well as 135 degrees, which is depicted here. I introduced a pair-wise orientational order correlation function, which calculated the order parameter between particles as a function of their separation. For disordered systems, we expect this to decay to zero over relatively short distances, although excluded volume interactions may result in some short-range ordering – as seen in blue here.

Ordered phase formation is characterised non-zero long range orientational order – here we observe system-wide order at longer times (corresponding to higher volume fractions in this contracting simulation).

Periodic structure would be expressed here in oscillatory aspects to the correlation function; unfortunately these were not conclusively observed over the length scales tested here. It is worth noting that the extend of the simulation region is rather limited (typically only 3 times the mesogen length in the concentrated phases) and so we might still expect periodic structures, particularly twisted nematic phases, occurring over a longer lengthscale than this.

**Dynamic Properties:** While the phase behaviour of rigid rods is well studied, much less is known about the dynamical properties. This in, in part, due to the traditional popularity of Monte Carlo simulation approaches, which cannot predict dynamic properties.

Here, I calculate the direction diffusion coefficients across a range of liquid crystal phases, which were identified using the order parameters discussed previously. Here, root mean squared displacement is plotted over time, expecting a linear relationship in logarithmic space, with the intercept corresponding to the diffusion coefficient.

The leftmost pair of plots, with the highest volume fraction phi, correspond to the smectic phase. Here, the motion between x − z layers (or along the y-axis) is restricted. The reduced gradient in this direction suggests sub-diffusive behaviour, with a reduced power law relation. The centre pair give the nematic phase, with preferential displacement along the y axis corresponding to a greater diffusion coefficient. Finally, the rightmost pair give the isotropic phase, with no preferential direction and isotropic diffusion. Note that there are no significant differences between the x and z directions in any phase, as these directions are equivalent in the phase structure.

These results demonstrate an alternative method for phase detection and characterisation through the measurement of direction dependant dynamic properties, such as the diffusion coefficients in this case.

# Conclusions

In this project I considered the phase behaviour of DNA nunchuck molecules, consisting of two sections of ds-DNA connected by a short section of ss-DNA. Based on a coarse-grained model of two rigid rods connected by a (semi-) flexible linker. I also introduced a simpler ‘rigid rod’ model, without the flexible linker, to verify the phase identification techniques used here.

**Primary Findings:** Simulations of rigid rods demonstrated the existence of a first-order isotropic–nematic phase transition, and verified Onsager’s across a range of aspect ratios, confining the critical volume fraction to within 5% of the theoretical value.

I then considered simulations expanding an initial crystalline phase, which confirmed the value of this critical volume fraction, and verified the equilibrium nature of this transition. Here, I also identified the formation of a smectic phase here, however further categorisation of the transitions associated with this phase is left for a separate work.

Application of the same techniques to the nunchucks system gave evidence for the formation of an ordered, quasi-nematic phase in this system, in both the fixed rigidity and fixed angle configurations. Finally, I demonstrated that the measurement of dynamic properties provide a little-studied alternative method to identify phase transitions and characteristic symmetries of such systems, providing conclusions in agreement with traditional methods based on the order parameter.

**Further Work:** While I have identified a quasi-nematic phase in this nunchuck system, I was unable to characterise the exact symmetry of this phase, and whether it possess additional symmetries to the conventional nematic phase. I believe that periodic aspects to this structure may occur over length scales larger than the simulation regions used in this project, and hope to use additional computational resources to illuminate such order over the summer.

The crude nunchuck representations used in this research may also be replaced through the introduction of a new interaction class in LAMMPS to fully replicate the intramolecular potential between the two arms of the nunchuck, derived by Jiaming from OxDNA.

Finally, I believe the application of dynamic properties to phase detection may be applicable more widely, and serve as a useful alternative to traditional methods, either as a secondary method of verification or in cases where traditional methods are unwieldy and less applicable.

*Thank for you listening, and I’d be happy to answer any questions you have!*