
Simulating Liquid Crystals

Kit Gallagher Supervisors: Prof Erika Eiser, Mr Jiaming Yu

March 24, 2021

The specificity of DNA base-pair interactions gives considerable functional control in the design of anisotropic nano-particles, enabling the formation of liquid crystal phases. This project aims to study the liquid phase behaviour of such non-conventional liquid crystal molecules, with a particular focus on the novel ‘nunchuck’ structure - two rigid rods connected via a flexible linker. The Eiser Group have previously considered intra-molecular interaction potentials at the single-nucleotide level for a single DNA nanoparticle, and I am now implementing these potentials in larger, more coarse-grained models of multiple nanoparticles, through open-source software LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator). Such systems are expected to form smectic (layered) phases at high volume fractions. THIS WILL BE EDITED AT THE END

1 Introduction

What are we studying? (brief) Why are we interested? Applications of this!
Outline of report

2 Background

2.1 Liquid Crystals

Include known phases etc

2.2 Onsager Theory

Introduce theoretical predictions to be validated later Mathematical derivations may be provided in appendices

2.3 Previous Computational Work

3 Methods

3.1 Simulation - LAMMPS Software

Detail how this works. Include description of natural units conversions etc

As introduced in Section 2.3, all molecular dynamics simulations were completed in LAMMPS. LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) is a medium coarse-grained, classical molecular dynamics code developed to replicate solid-state materials and soft matter mesoscopic systems [1, 2].

It should be noted that a system of natural units are used throughout this paper. Based on the Lennard-Jones potential, the cut-off length and characteristic energy are set to unity.

The physical values for a system may be considered for a specific system (in this case strands of ds-DNA) through scaling via the relevant mass, length scale and energy scale of this system. However the dimensionless simulations presented here may be applied to any similarly-shaped mesogens; we would expect other systems to display the same behaviour over a timescale determined by their material properties [3].

3.2 Simulation Molecules

As introduced in Section X, we are considering ‘nunchuck’ molecules formed of two rigid rods connected by a flexible linker, as depicted in Figure 1a. However, as the interaction potential of an anisotropic particle is rather complex, it is computationally simpler to consider each molecule as a system of connected spheres, each with a separate isotropic interaction potential (detailed further in Section 3.3).

This is visualised in Figure 1b, for rigid rods of aspect ratio 7. The ss-DNA is represented by a further

The nunchucks are formed of two rigid rods of ds-DNA, connected via a flexible linker of ss-DNA, and the complete nunchuck is modelled as a rod of 60 base pairs long. With the standard values for DNA of radius $r = 2\text{nm}$ and length (per base pair) of $l = 0.33\text{nm}$, we obtain an aspect ratio of 10 for this rod. Within LAMMPS, this is expressed as ten spherical balls (aspect ratio 1) bound rigidly together in a linear structure.

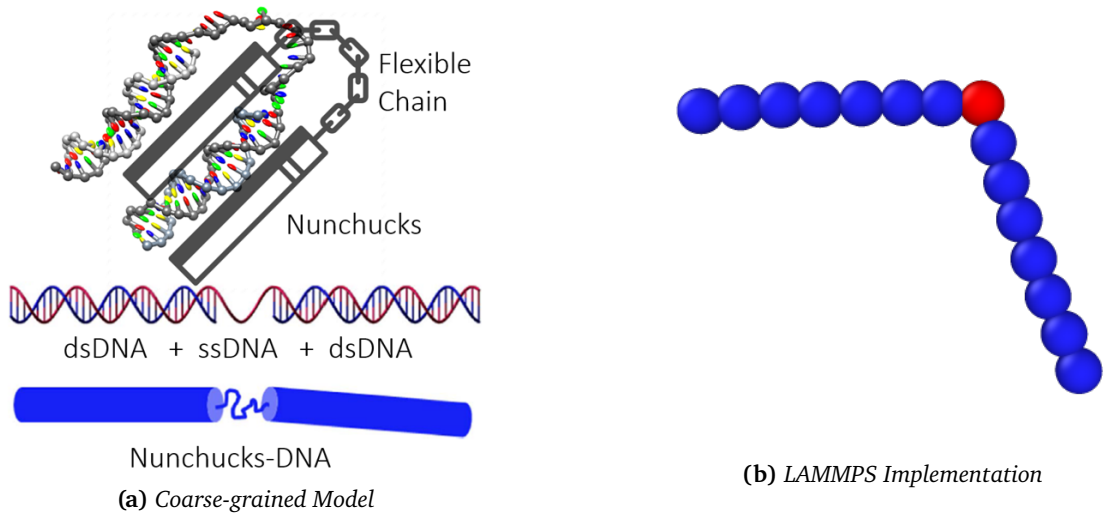


Figure 1: Depiction analogy between the DNA mesogen and the nunchucks. Note the appearance of the flexible ss-DNA linker between the rigid ds-DNA rods, and the implementation within LAMMPS on the right. The central red sphere is given modified bond properties to replicate the nunchuck’s flexibility. Figure (a) created by Jiaming Yu (Eiser Group, Cambridge).

It is worth noting that the persistence length of DNA is around 50nm [4], so the approximation of perfect rigidity is valid over the length-scale of the molecule.

3.3 Intermolecular Potential

parameters and potentials used etc. Timescales and simulation sizes used etc

A shifted, cut-off Lennard-Jones potential was chosen to represent pair-wise interactions between molecules. While the Lennard-Jones potential [5, 6] has long been the natural choice for molecular dynamics simulations [7], its infinite range introduces computational complexity as interactions between all pairs of particles must be considered. It is therefore increasingly common to use a cut-off version, whereby the potential is set to zero beyond a ‘cut-off’ radius, and here we chose to neglect the entire attractive tail. As well as simplifying the calculations required, this also allows our results to be generalised to any mesogens without attractive inter-molecular forces (that typically favour ordered-phase formation), as any phase transitions observed here must be purely entropically driven. This is commonly known as a soft-core model, where particle overlap is suppressed via this repulsive potential rather than any excluded volume interactions, and is computationally much less demanding [8, 9].

However, this cut-off may cause unphysical behaviour if the potential does not tend to zero smoothly at this point. This is remedied by the addition of a constant term, described in the full form of the pair-wise potential U_{ij} in (1):

$$U_{ij} = 4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right] + \epsilon \quad r_{ij} < r_c = 2^{1/6}\sigma \quad (1)$$

Here σ and ϵ are the relevant length and energy scales of the system, formally corresponding to the particle separation at which the $U_{ij} = 0$, and the depth of the potential well. It is worth noting that the effects of this truncation and shift on the overall thermodynamic quantities are well documented [10, 11], and changes in lyotropic properties are negligible in 3D bulk liquids with a conserved particle number [12].

3.4 Analysis

Includes custom written python scripts and OVITO freeware. Credit scripts written by other group members.

4 Rigid Rod Simulations

5 Nunchuck Simulations

6 Conclusion

Summarise key results from above, and emphasise their importance Also give limitations of results obtained, and suggest direction for further work

References

- ¹S. Plimpton, “Fast parallel algorithms for short-range molecular dynamics”, *Journal of Computational Physics* **117**, 1–19 (1995).
- ²*Large-scale atomic/molecular massively parallel simulator*, Sandia National Labs, (Mar. 2020) <http://lammps.sandia.gov>.
- ³D. C. Rapaport, *The art of molecular dynamics simulation* (Cambridge University Press, Apr. 2004), pp. 13–15.
- ⁴H. G. Garcia, P. Grayson, L. Han, M. Inamdar, J. Kondev, P. C. Nelson, R. Phillips, J. Widom, and P. A. Wiggins, “Biological consequences of tightly bent DNA: the other life of a macromolecular celebrity”, *Biopolymers* **85**, 115–130 (2007).

- ⁵J. E. Jones, “On the determination of molecular fields.— I. From the variation of the viscosity of a gas with temperature”, *Proceedings of the Royal Society of London. Series A, Containing Papers of a Mathematical and Physical Character* **106**, 441–462 (1924).
- ⁶J. E. Jones, “On the determination of molecular fields. — II. From the equation of state of a gas”, *Proceedings of the Royal Society of London. Series A, Containing Papers of a Mathematical and Physical Character* **106**, 463–477 (1924).
- ⁷S. Stephan, M. Thol, J. Vrabec, and H. Hasse, “Thermophysical properties of the Lennard-Jones fluid: database and data assessment”, *Journal of Chemical Information and Modeling* **59**, 4248–4265 (2019).
- ⁸G. V. Paolini, G. Ciccotti, and M. Ferrario, “Simulation of site-site soft-core liquid crystal models”, *Molecular Physics* **80**, 297–312 (1993).
- ⁹Z. E. Hughes, L. M. Stimson, H. Slim, J. S. Lintuvuori, J. M. Ilnytskyi, and M. R. Wilson, “An investigation of soft-core potentials for the simulation of mesogenic molecules and molecules composed of rigid and flexible segments”, *Computer Physics Communications* **178**, 724–731 (2008).
- ¹⁰S. Stephan, J. Staubach, and H. Hasse, “Review and comparison of equations of state for the Lennard-Jones fluid”, *Fluid Phase Equilibria* **523**, 112772 (2020).
- ¹¹K. R. S. Shaul, A. J. Schultz, and D. A. Kofke, “The effect of truncation and shift on virial coefficients of lennard-jones potentials”, *Collection of Czechoslovak Chemical Communications* **75**, 447–462 (2010).
- ¹²B. Smit and D. Frenkel, “Vapor–liquid equilibria of the two-dimensional lennard-jones fluid(s)”, *The Journal of Chemical Physics* **94**, 5663–5668 (1991).

Appendix A Onsager Theory

Appendix B Netamtic Order Parameter

include theoretical derivation and calculation

Appendix C Code?