Monte Carlo Simulation for the Onsager Model of the Nematic-Isotropic Phase Transition in Liquid Crystals

A Final Project in Condensed Matter 2

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Please note that this project is based entirely on knowledge acquired in the course Condensed Matter 2 and other previous courses like Statistical Mechanics and Numerical Methods, so although some reading of articles and relevant books was done previous to the writing of this project and the algorithm itself, it eventually proved unnecessary in order to complete the project. For that reason, a reference section is not included.

Introduction

Liquid crystals could sometimes be regarded as an ensemble of rigid rods (with length l in the major axis, also referred to as the molecular axis, and diameter d in the minor axis), representing long molecules with no polarity (a reflection of a rod relative to its center will have no effect on interactions with other nearby rods or external fields). Two of the common phases of such an ensemble are the isotropic phase and the nematic phase.

The isotropic phase is characterized by a uniform angular distribution of the rods' orientation in space, whereas in the nematic phase, the rods tend to align with a preferred direction (the director). The spontaneous alignment of the system could be achieved when the system concentration is increased. With increased concentration, entropy related with the rods' freedom of translations in space becomes dominant relative to entropy due to different orientations of different rods. In other words, there is a tradeoff between entropy of translations and entropy of rotations. The phase of the system could also depend on other physical effects related to the free energy of the system that are beyond the scope of this project, such as the interaction with an external electromagnetic field or interactions between the molecules themselves (that could depend in the relative angle between molecules).

The phase of the system could be described by an order parameter from which an expression for Landau's free energy could be constructed for the system. In the case of the Nematic-Isotropic phase transition of a 3 dimensional system, the scalar order parameter is:

$$S = \left\langle \frac{3\cos^2\theta - 1}{2} \right\rangle = \langle P_2(cos\theta) \rangle \quad (1)$$

Where θ is the angle between the liquid crystal molecular axis and the local director, and the brackets denote both a temporal and spatial average. P_2 is the second order Legendre Polynomial. In the Isotropic phase, where θ is uniformly distributed, the value of the order parameter is 0, whereas in a certain concentration, in which the molecules start to align with the local director, its value jumps to a finite value. A perfect nematic phase is represented by $S = 1$ ($\theta = 0$ for all molecules).

One of the simplistic models for the nematic–isotropic phase transition is the Onsager hard-rods model, proposed by Lars Onsager. This theory considers the excluded volume around the center of one idealized cylinder as it approaches another (see fig 1). In case of parallel rods, the excluded volume is the smallest, meaning that the center mass of each of the examined rods has a lot more space around it to which it could be translated to. If however, the rods are perpendicular to one another, the excluded volume is the largest, and there is a lot more space forbidden for translation. In the limit of the $L \gg d$, the excluded volume is given by:

$$V_{exc} \approx 2L^2 d|sin\gamma| \quad (2)$$

Where γ is the relative angle between the molecular axes of the two rods.

This project aims to simulate the change in the order parameter S with respect to change of the system concentration (number of rods per unit volume) in a two dimensional system with no external fields and no molecular interactions beside the fact that the rods are hard. In a two dimensional system we should construct a new scalar order parameter as follows:

For a system with rods, each with a molecular axis

$$\hat{l}_i = (cos\alpha_i, \sin\alpha_i) \quad (3)$$

Where α_i is the angle of the i-th rod relative to the x axis, we define

$$\overleftrightarrow{T} = \langle \hat{l} \otimes \hat{l} \rangle \quad (4)$$

The brackets denote the same average as in (1). This way, we get for the isotropic phase

$$T_{ij} = \frac{1}{2}\delta_{ij} \quad (5)$$

Where δ_{ij} is the familiar Kronecker's delta in two Dimensions. For a perfect alignment of all rods in the x direction:

$$\overleftrightarrow{T} = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \quad (6)$$

We can now construct a tensor order parameter that vanishes for the isotropic phase as follows:

$$\overleftrightarrow{Q} = 2\overleftrightarrow{T} - \overleftrightarrow{I} \quad (7)$$

Here, $\overleftrightarrow{Q}$ is a traceless, symmetric $2 \otimes 2$ matrix, exactly as the in the familiar order parameter for the 3 dimensional case, and we are free, of course, to rotate $\overleftrightarrow{Q}$ to the base of the system's director and another base vector perpendicular to it. The corresponding scalar order parameter of the two dimensional system would then be:

$$S = \langle 2\cos^2\theta - 1 \rangle \quad (8)$$

Where θ is the angle relative to the system's director. Therefore, S vanishes in an isotropic phase and equal to unity in a perfect nematic phase in which all rods are parallel to the director.

In the two dimensional case we can also neglect d and imagine that the rods have only one dimension (the length l in their molecular axis) and no width at all ($d \to 0$, this of course, is something we can only get away with in the 2D case). In this case the potential between two rods i and j, is given by:

$$V_{ij} = \begin{cases} \infty & rods\ intersect \\ 0 & otherwise \end{cases} \quad (9)$$

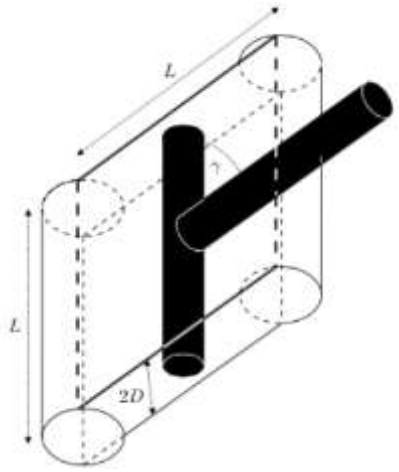


Fig.1 – Excluded volume around a rod's center "seen" by another approaching rod with a molecular axis in angle γ relative to the first rod's molecular axis. Both rods are of length L in their molecular axis and width d in their minor axis

The Algorithm pipeline

The steps of the simulation for each set of parameters (system width(L_x), system height (L_y), number of rods(N), rods lengths (l), and number of iterations(T)) are as follows:

a. First, the system is being initialized and for N rods, the program draws locations and angle. For this stage, the locations were drawn based on a uniform distribution within the system boundaries (with the condition that rods centers of masses could not overlap). For the angle of each new rod, the program finds neighbor rods that could potentially intersect with the new rod, and calculate the interval of angles allowed for the new rod so that it won't intersect any of its neighbors. The angle for each new rod is then drawn (uniformly) from the allowed angles interval.
b. After the system had been initialized, the program preforms T iterations. Each iteration tries to change the system by the Metropolis Monte Carlo algorithm:
Each of the iterations iterates over all rods (with a random order) and tries to change each rod's location and angle. First, a translation for the rod's center of mass is being drawn from a normal distribution (under a normal distribution both in the x axis and y axis, each point on an arbitrary circle with radius r around the original location, will have an equal chance of being selected). Then, if the new location is valid (not on any of the other rods, and not outside the system boundaries in the case of hard walls), the allowed angles interval is calculated and a new angle is being drawn from it (uniform distribution).

Note that in the Metropolis Monte Carlo process, all possible states should be considered while drawing a new state for one molecule and the step is accepted in a probability proportion to its Boltzmann factor. In our case though, the Boltzmann factor is either 0 (if rods intersect) or 1 (if rods do not intersect) and therefore the angle could be drawn from the allowed angles interval (instead from $[0, \pi]$) to increase the number of accepted steps and drive the system to equilibrium faster.

c. The above process (described in a, b) repeats for different concentrations (changes with L_x, L_y). For each concentration, the output order parameter is regarded as the order parameter after all iterations are done. The rationale behind taking the last value, is the expectation that after all iterations, the system is the closest to equilibrium and the order parameter is a good representative of a system in equilibrium given its concentration.

The simulation was executed twice, under two different boundary conditions – once for periodic boundary conditions and once for hard walls boundary conditions.

The algorithm output

For each concentration, the program plots the following:

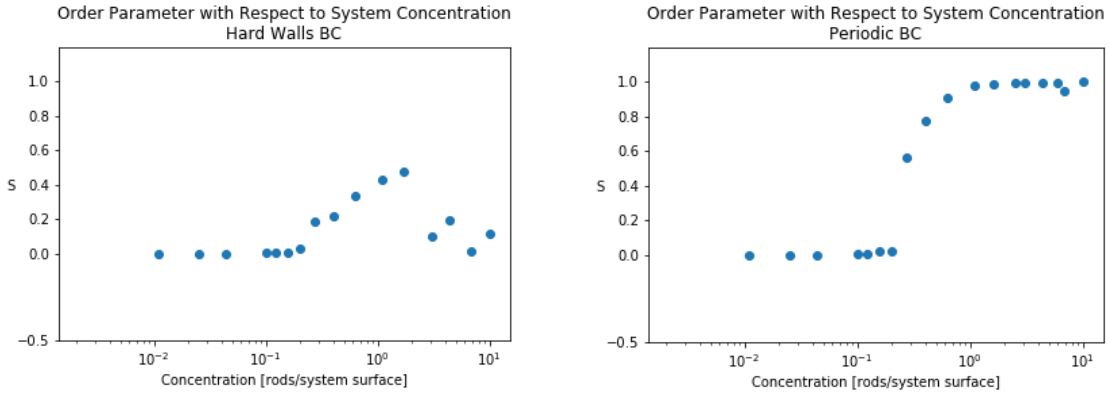
1. The space itself (all rods in the system plotted on an x-y plan)
2. A heat-map of the order parameter with respect to location in space. This plot is important because sometimes the order parameter of the whole system indicates that the system is in the isotropic phase, while it is actually fragmented to different areas, each is deep within the nematic phase but with a different local director from that of other areas of the system, also within the nematic phase with their own local director (as will be demonstrated in the results).
3. Relaxation time plot – correlation between directors of systems separated by τ iterations:
   $\langle \widehat{n_i} * \widehat{n_{i+\tau}} \rangle$ with respect to τ. Where $\widehat{n_i}$ is the direction of a vector with an angle equal to the average angle of the system relative to the x axis in the i-th iteration. This plot helps to understand how many iterations are needed for the system to change relative to initial state and move towards equilibrium. For small τ, the correlations are ~ 1, wheres for a large enough τ, we expect the system to rotate and the correlations to drop.

After the program had been executed for all concentrations, it plots a graph of the order parameter with respect to the system concentration given by $\frac{N}{L_x * L_y}$.

All figures are saved in a designated folder created in the scripts path (see user guide).

Results

Executing the algorithm for several different concentrations (for a square system in which $L_x = L_y$), with $N = 1000,\ l = 5,\ \mathrm{T} = 2000$, yields the following results:



a *b*

Fig.2: a. The Order Parameter with respect to system concentration for the hard walls case. b. same for the periodic boundary state case. In both cases the order parameter was calculated globally – over the whole system. It is possible to see that we get the expected behavior for the periodic boundary conditions while the hard walls simulation shows an increase in order parameter from certain concentration, but ultimately drop to low values of the order parameter at high concentration

Looking at the results for the system order parameter with respect to its concentration (Fig 2), it seems that for the periodic boundary condition, the simulation yields the expected behavior – low values of the order parameter at low concentration and then a sudden increase, at a critical concentration of $c \approx 0.25$, to high values. However, the results for the hard walls case are not as expected. While calculating the order parameter of the whole system, we get a significantly smaller increase around the same critical concentration we got from the periodic case, and when the concentration goes to even higher values, the order parameter starts to decrease back to low values. Thus, we go to higher resolutions and examine whether the system contains different areas with nematic phases (with different director) or if it contains just one phase – isotropic everywhere and in every scale. For that we can examine the system plot directly, for certain concentrations (see Figure 3, 4).

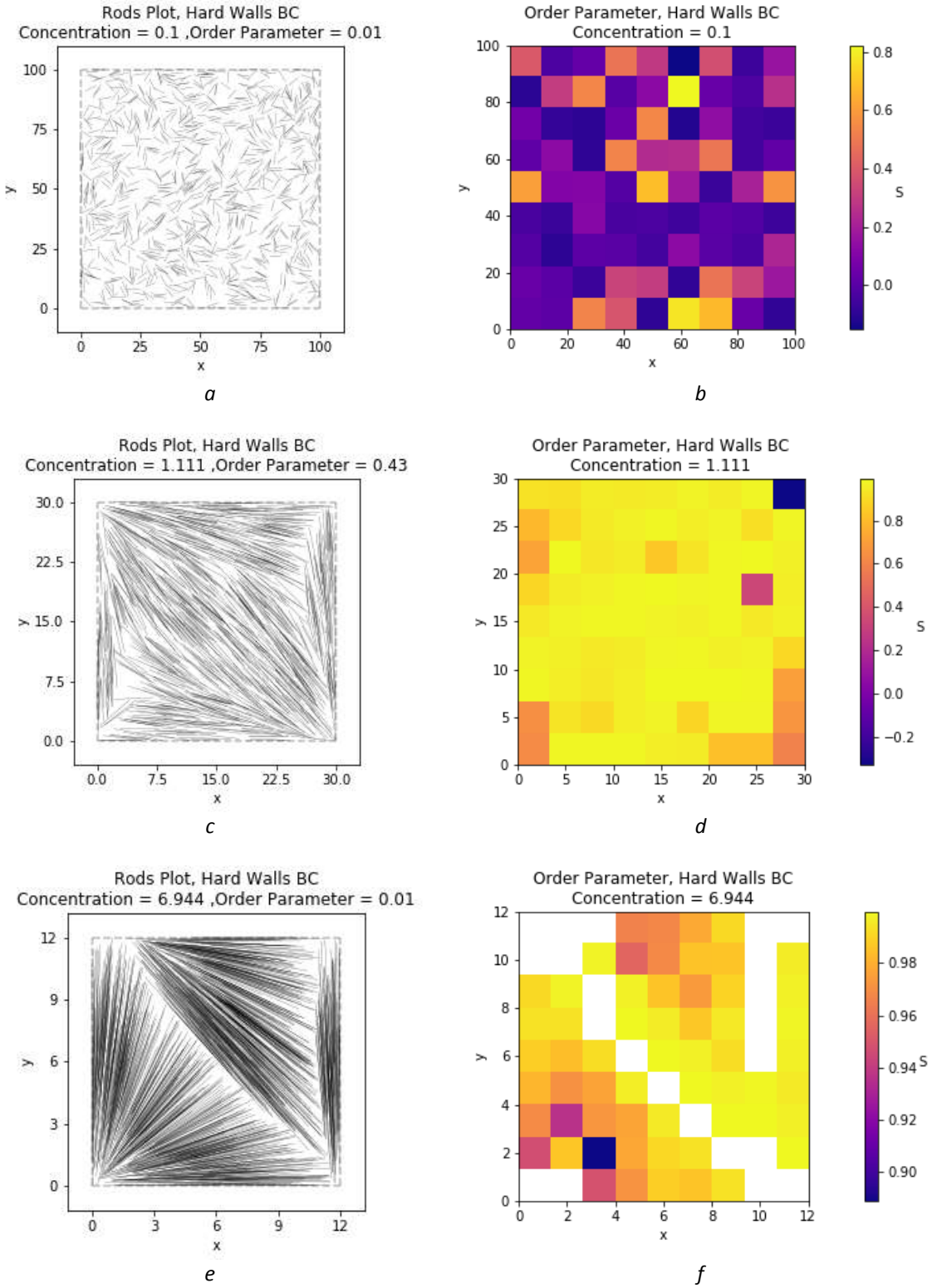


Fig. 3. a, b – system plot and order parameter heat-map for different sub-squares in a hard-walls system with concentration = 0.1, respectively. c, d – same for concentration = 1.111. e, f – same for concentration = 6.944. It is possible to see that in higher concentrations, rods tend to align with their neighbors and form a localy nematic phase in different separated areas. Globally the system is not in the nematic phase because it is constructed from different "nematic" areas with different local directors.

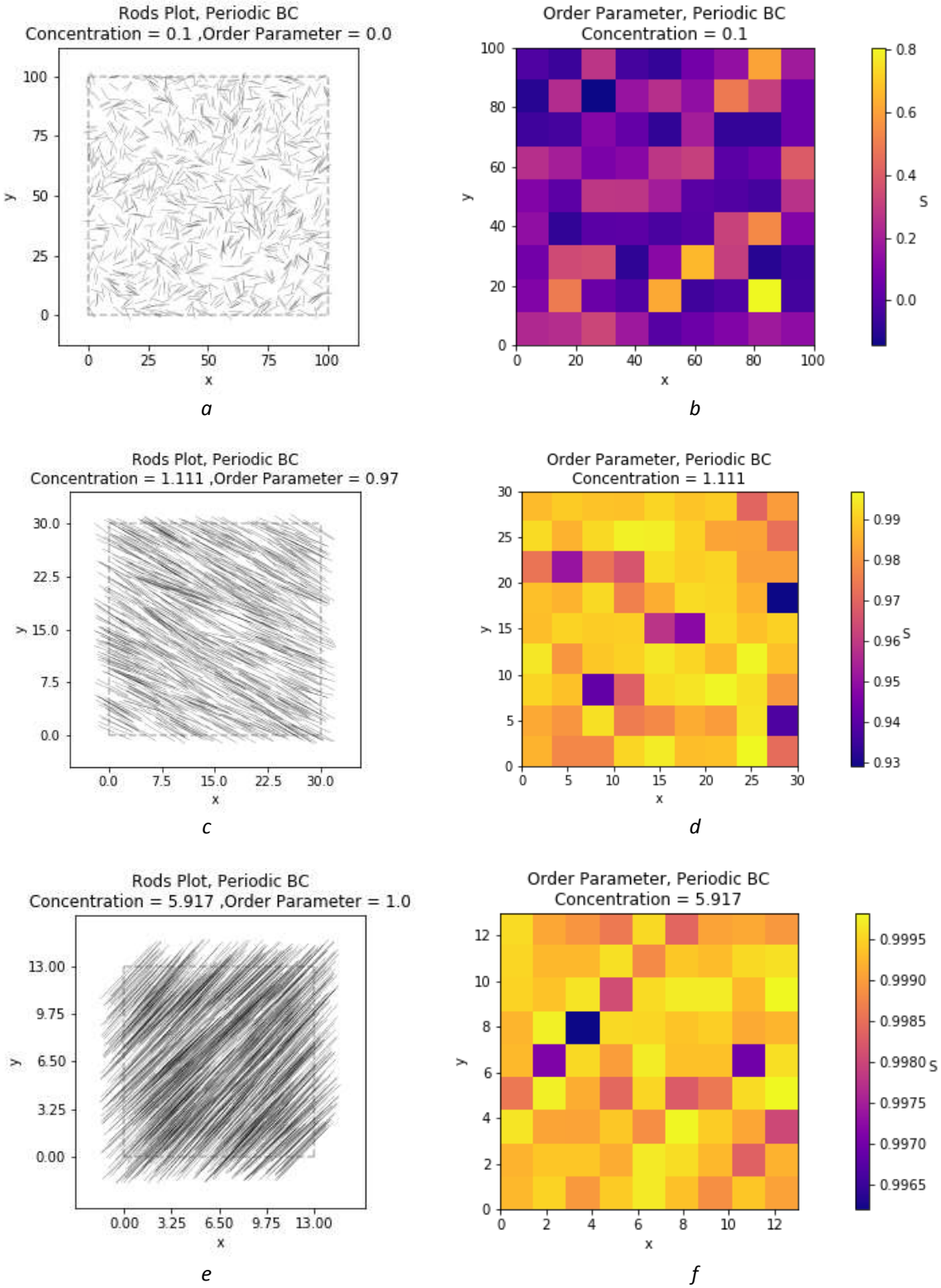


Fig. 4. a, b – system plot and order parameter heat-map for different sub-squares in a periodic system, respectively for concentration = 0.1. c, d – same for concentration = 1.111. e, f – same for concentration = 5.917. we can see that for the periodic case, the system behaves as expected in a global scale, and given enough time, all the rods will align together.

It is possible to see that in low concentration, the system is in the isotropic phase, although there are few areas in which it seems that few rods stack together and form a somewhat nematic region - in some areas the order parameter climb to ~ 0.7 (see Figures 3a, 3b and 4a, 4b). The effect of coexistence of the two phases is predicted by the Onsager model, but the suspected "nematic" regions mentioned, do not contain many rods so we could not conclude that this effect is clearly demonstrated in this simulation - there are no large enough regions characterized by a high value of S and containing a large enough number of rods. It is also possible to see that while concentration increases, the rods tend to align with their neighbors. In an intermediate concentration (such as in Figure 3.c\d and Figure 4.c\d), the correlation between the molecular axes of different molecules in a system with hard walls, is high upon short ranges, but decrease upon large ranges. Moreover, although in high concentrations the system is globally isotropic (see Fig 2), it is possible to see that it is constructed from sub-regions, each is deep within the nematic phase ($S \sim 0.9$, when calculated locally, considering only molecules in the sub-region) but with a different local director than that of other, separated sub-regions. The difference between the two boundary state lies in the fact that while in the periodic case, possible angles of rods close to one edge of the system would be influenced from the orientation of rods in the counter edge, and given enough time (iterations) all the rods will align together. In the case of the hard-walls system though, rods close to the walls are constrained by them, and will tend to align parallel to the close wall. Different part of the hard-walls system then, could get stuck aligned with some local director that would be determined mostly by the wall "direction". This local director is actually perpendicular to other local directors determined by perpendicular walls. The system then will be divided to different nematic areas forever, no matter how many iterations would be executed.

An interesting result we get for the periodic boundary system is that even in very high concentrations, we can expect spontaneous symmetry breaking and find regions of rods stacked close together, aligned with a direction different from the general direction of the system around them (See fig 5).

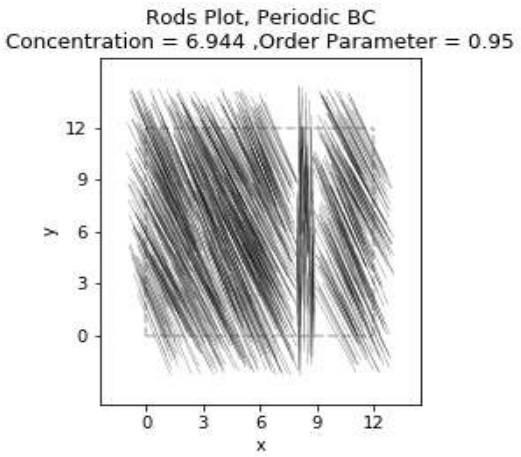
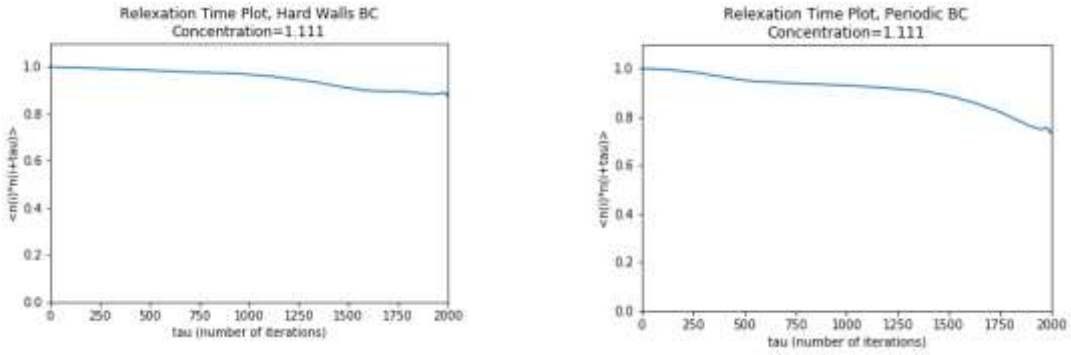


Fig 5. Rods plot for a periodic system in concentration = 0.6944. We can see a region in which a group of rods of rods are aligned with a direction different from the general direction of the system.

We can also examine the relaxation time of the two simulations – the number of iterations in the Metropolis process needed for the system to change as defined in the "The algorithm output" section. If the correlations between the directors of systems separated by many iterations are preserved, we can conclude that the system might be stuck in some state or the angular distribution is uniform for all iterations (see Figure. 6).

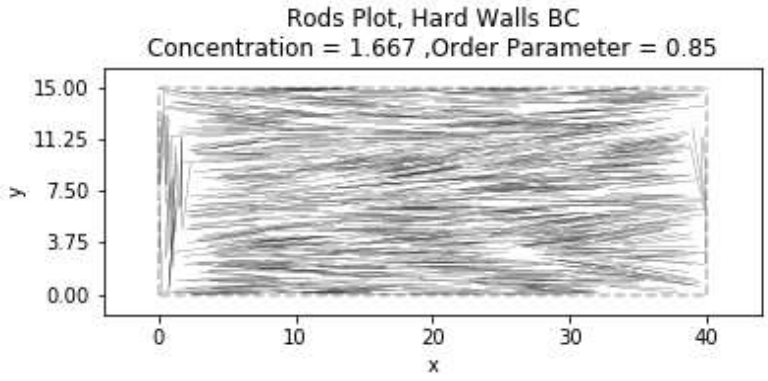


A *b*

Fig 6. A relaxation time plot for the hard-walls system. b. relaxation time for the periodic system. It is possible the see that correlation between the hard walls system directors are preserved for longer, and many more iterations could be needed in order for it to be able to get to an equilibrium.

The relaxation time plots (Fig 6), indicate that correlations between directors of the hard walls system are preserved for longer (correlations in the periodic system drop faster). Meaning, it could take many more iterations for that system to change relative to its initial state and reach equilibrium. The relaxation time as defined, is probably a good estimator for the system change in intermediate concentrations only. In low concentrations, we expect a uniform angular distribution in all iterations no matter how the system changes. In extremely high concentrations, it might even be impossible for a hard-walls system to reach a global nematic phase, given the initial state contain different nematic regions with different local directors. In extreme concentration then, the relaxation time plot would show a flat line. Still, this might not be true for concentrations in an intermediate range, in Fig. 6 for example, we can see that in the last iterations, the system still changes and correlations are in a downward trend. If the simulation would go beyond 2000 iterations, both boundary states systems might still change and correlations would continue to drop with τ. For the periodic system that could just mean a rotation of the system director (with all the rods aligned with it at any iteration), but for the hard walls system that could mean a stacking of more and more rods together, and alignment with a specific director.

Another interesting thing we can examine with the hard-walls system, is the effect of different shapes of the system. It is expected that if $L_x > L_y$, and the concentration is high enough, the system will favor an alignment with a director pointing in a direction somewhat parallel to the x axis, except in the area of the vertical edges, close to which the system will favor alignment with the y axis. This behavior exactly is depicted in figure 5, representing the algorithm results for a systems in which $Lx > Ly$ (see Fig. 7).



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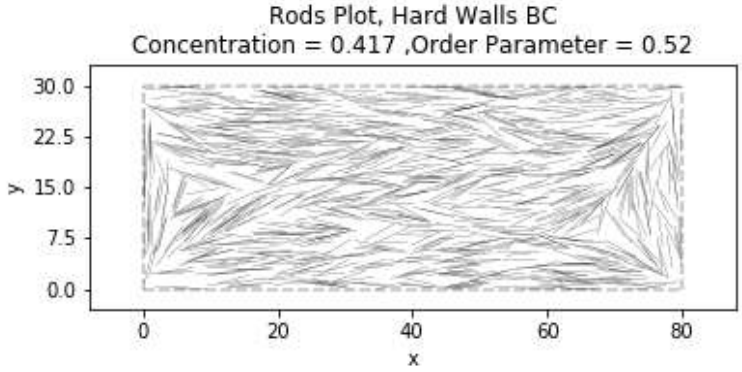

b

Figure 7 – system plots for $L_x > L_y$. a. for concentration = 1.667, b. for concentration = 0.417. As expected, most of the system is aligned with the x axis. A small portion of the molecules, close to the walls parallel to the y axes, are aligned with the y axis and causing a splay.

Conclusions

This project examined and illustrated the Onsager model for the isotropic-nematic phase transition of liquid crystals in two dimensions, using Monte Carlo method. For a system with periodic boundary conditions, we got the expected behavior. For a system with hard walls, it has been shown that even though the expected behavior of the order parameter with respect to change in concentration was not achieved for a global examination of the system. Instead, the system went through "fragmentation" while the concentrating increased and was divided to sub-regions, each in its own is within the nematic phase. For the hard-walls system, we also achieved the expected alignment of the system with the direction of large walls when the walls were not in the same size. In low\intermediate concentrations, the results were somewhat similar for both periodic and hard-walls boundary conditions, indicating that the number of rods chosen for this simulation was sufficient to simulate a large enough system in those concentrations. For high concentrations though, the systems behaved differently, indicating that 1000 rods were not enough, as if it were, we shouldn't have expected such a difference in behavior due to different boundary states.

It is worth mentioning, that if memory and computational resources are not a problem, it is probably better to choose a different calculation for relaxation time in a manner that saves each iteration results for all rods positions and angles. That way, it is possible, and probably more accurate, to calculate correlations between local directors over τ iterations.
Also important to mentation is the fact that we did not really capture the state of coexistence of the two phases as predicted by the Onsager model. It is possible that 1000 rods were insufficient for demonstrating this effect. Symmetry breaking over short distances did occur, and in the case of hard walls boundary conditions, we could even notice a splay over a range between two nematic regions characterized by different local directors.
Algorithmic efficiency was not a part of this project, but It should be noted that if this simulation is to be executed with a much larger number of rods, or for a larger number of iterations in the Metropolis Monte Carlo process than those used for the simulations presented in this project, two minor but essential improvements would have to be implemented. First, instead of storing all the rods in one matrix, it could be useful to store them in a hash table, in which every key points to a different region in space and thus to a sub-matrix containing all of the rods located in that region. That way, finding the neighbors which could potentially intersect each rod will not require N calculations for each step, but much less. Second, if computational resources are not a problem, it is recommended to use parallel processing to run the simulations for the different concentrations at the same time, (the simulations for different concentrations are of course independent).

User guide

In order to run the simulation, please follow those steps:

1. Install python 3.6 (or a more recent version of python3). Make sure to add python to PATH (the environmental variable in your operating system)
2. Extract the .py files supplied in the scripts folder included in this project to your preferred directory
3. Open Onsager_MC_Params.py file and set simulation parameters (see parameters description bellow)
4. Open the command prompt (for windows users) or shell (for Unix\Linux users) and navigate to the .py files directory (the directory chosen in step 2)
5. For simulation using hard-walls boundary conditions, run the command:
   python onsager_nematic_isotropic_mc_hard_walls.py

   For simulation using periodic boundary conditions, run the command:
   python onsager_nematic_isotropic_mc_periodic.py

The program will print its progress to shell – each new simulation (new concentration and system dimensions) will be announced when started. For each iteration, number of excepted steps, order parameter and mean angle relative to x axis will be printed.
If you are using Unix, it is recommended to use screen command and run the simulation on a child terminal (especially for long simulations).

Benchmark: $\sim$1 hour for 1000 rods in a concentration $\sim$0.6, with 1000 iterations (for a standard home\office computer). for high concentrations (~ 10) the simulation should take several hours.

Parameters Description

The following variables should be defined by the user in the Onsager_MC_Params.py file supplied with this project before executing the simulation

Variable name	description	Type
rods_n	Number of rods in the system	Int
rod_l	Length of each rod in its molecular axis	Int/float
iterations	Number of iterations for the Metropolis process. After space is initialized, each iteration will go through all rods and try to change their location and orientation based on the metropolis algorithm	Int
factor_sd_normal	This variable controls how far could a new rod's location be relative to its original location in each of the metropolis steps. The program will try to draw a translation in the X-Y plane, for each base vector the translation will be drawn based on a normal distribution with SD of factor_sd_normal*(Lx+Ly)/2	Int/float
Lx_arr	Lists of Lx, Ly dimensions for each simulation. Lists should be the same size. Each simulation will take one value from each list in order to determine system size (and boundaries) and concentration. The i-th simulation will take Lx (x dimension) to be Lx_arr[i] and similar for Ly.	Lists of Ints\floats
Ly_arr		