MENG 255 Final Project

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1 Introduction

The nematic to isotropic phase transition in a liquid crystal system is characterized primarily by a transition from the liquid crystalline to pure liquid state. In the liquid crystal mesophase, liquid crystal molecules display properties of both crystalline solids and pure isotropic liquids, that is, they have the translational freedom of a liquid, but experience an "orientational freezing", a general alignment along one direction[1]. We define this alignment using the "director", which is the average direction in which the molecules are pointing. The liquid crystals we are modeling are symmetric along their long axes, so for the director we have $-n = n$. This average is not known a priori, and in our later Monte Carlo simulations we will not be imposing an ideal order onto our system,so the best way we can determine the relative order of our system is using a second rank order tensor, defined as:

$$Q_{\alpha\beta}(\vec{r}) = \frac{1}{N}\sum_{i}(u_{\alpha}^{(i)}u_{\beta}^{(i)} - \frac{1}{3}\delta_{\alpha\beta})$$

Where α and β represent components x, y, z of the Cartesian unit vector representing our liquid crystal molecules[2]. From this tensor, we can determine a scalar order parameter, defined as:

$$S = \langle P_2(cos\theta_n)\rangle = \langle\frac{3cos^2(\theta_n) - 1}{2}\rangle$$

Which will be the the largest eigenvalue of a diagonalized order tensor multiplied by $\frac{3}{2}$[3].

The transition from the nematic to isotropic state is a weakly first order transition, which we will note through a sudden, drastic change in the slope of the internal energy of the system at the critical point. Additionally, we can mark this phase transition through a similar discontinuity in the order parameter, as an ideal liquid crystal simulation would transition from having some order to have no order, that is, from having a scalar order parameter between 0.6-1.0 to having a scalar order parameter of 0. The accuracy of this quantity is limited by the finite size of the system, so we should expect some error in the observed order parameters, but should still see a sudden, large jump in the scalar order[3].

2 Lebwol-Lasher Model

The Lebwol-Lasher model provides a simple, but fairly accurate representation of liquid crystal molecules which undergo a simple nematic to isotropic phase transition. It models the liquid crystal as a series of headless unit vectors, representing our rod-shaped molecules, placed on a simple cubic lattice that interact using the following potential[4]:

$$E = -\epsilon\sum_{\langle ij\rangle}P_2(cos\theta_{ij}) = -\epsilon\sum_{\langle ij\rangle}(\frac{3}{2}cos^2\theta_{ij} - \frac{1}{2})$$

This equation denotes the energy for a single lattice point at any given time - we sum the interaction potential, which is the second Legendre polynomial of $cos\theta_{ij}$, over all nearest neighbors, which will be the 6 lattice points connected to the lattice point of interest. This potential is determined from a mean-field theory liquid crystal model developed by Maier and Saupe, which accounts for the symmetrical nature of the molecules and reduces the interactions between them down to a simple interaction potential[5]. This potential can be visualized in Figure 1.

We can see that energy is minimized at $\theta = 0$ and $\theta = \pi$, which is when the liquid crystal molecules are perfect aligned with one another. This is desirable, if our system is receiving no energy, that is it is at $T = 0$, our molecules will all be perfectly aligned and thus in the crystalline phase as we would expect for low temperatures. This potential also accounts for the symmetry of the liquid crystal molecules, as $E_{\theta=0} = E_{\theta=\pi}$.

As stated earlier, the Lebwohl-Lasher model approximates a liquid crystal fluid as a series of liquid crystal molecules placed on a simple cubic lattice. The molecules are given full rotational freedom but no translational freedom, so all simulation steps and transformations are undergone along the rotational axes of our approximated

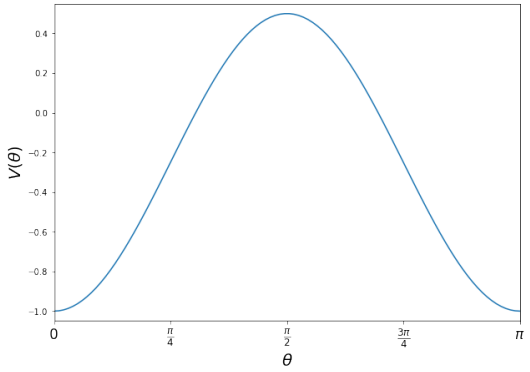

Figure 1: A graphical representation of the Lebwohl-Lasher potential from 0 to π.

liquid crystals. Through this model, a weakly first-order phase transition is seen at the critical temperature of $\beta\epsilon = 0.890 \pm 0.005$ (Where epsilon is the maximum interaction energy and $\beta = \frac{1}{T}$)[4].

3 Implementation

First, we want to properly initialize our lattice. I did so in one of two methods - either a uniform, that is frozen, initialization, or a random, that is isotropic, initialization. For the uniform initialization, all points are initialized as cartesian unit vectors pointing along the z-axis, $[0, 0, 1]$. For the random initialization, each lattice site is initialized and run as a cartesian unit vector on the unit sphere. We generate points on the unit sphere using the following equation:

$$vec = \frac{1}{\sqrt{x^2 + y^2 + z^2}} \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

Where $\begin{bmatrix} x \\ y \\ z \end{bmatrix}$ represents a vector of three points drawn from a standard normal distribution[9]. We will use the same equation for the random reorientation of molecules during our metropolis equilibration.

In the original paper by Lebwohl and Lasher, and it most papers following it, a simple Metropolis algorithm is used to equilibrate the lattice at varying temperatures to determine the nature of observable quantities at the phase transition[3][4][6][7]. For our initial trial of this system, we will do the same, following a simple Metropolis "lattice pass" algorithm, in which we will run the following steps for each lattice site (a lattice pass in this case refers to the number of steps required to reach all lattice sites).

1. Determine the initial energy of the lattice site using the sum of the Lebwohl-Lasher potential for the six nearest neighbors of the lattice site
2. Randomly reorient the lattice site vector to a random direction within the unit sphere
3. Determine the new energy of the lattice site
4. Accept or reject based on the Metropolis conditions

Doing this for several lattice passes, at least 1000 for points far from the transition temperature, will equilibrate the system to the desired temperature and allow us to begin to determine quantities for the observables. At temperatures near the transition, that is between about $\beta = 0.85$ and $\beta = 0.95$, at least 2000 lattice passes are required for equilibration due to "critical slowing down" within the system. At temperatures near the transition, both the nematic and isotropic states are present, and it takes the system a much longer time to reach its equilibrium configuration[8]. Additionally, the variance at these temperatures is higher. It is important to note that periodic boundary conditions are used for the determination of the energy of each lattice site.

4 Results

After equilibrating our system at various temperatures based on the directions outlined above, we return the following outputs for our observables. To start, let's look at the internal energy of the system as a function of β

We can see, as expected, there is a sharp drop in our energy and a sudden, dramatic change in the slope of energy as a function of temperature. Due to finite-size issues, we do not see a complete discontinuity in the energy as one should for a first order phase transition, but for the Lebwohl-Lasher approximation this is a satisfactory output for the system energy at varying temperatures. Remember that β is the inverse of temperature, so this graph shows the progression of system energy from high temperatures to low temperatures. We can see that the system energy decreases as temperature increases, with this magnitude of the slope of this decrease growing after the phase transition from nematic to isotropic. This is what we would expect, as at higher temperatures, our algorithm is much more likely to accept moves to higher

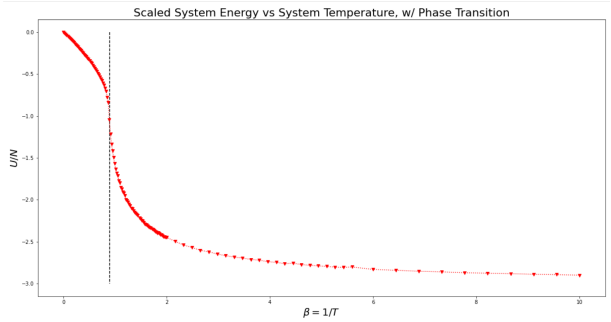

Figure 2: System Energy vs thermodynamic β. A first order phase transition can be see at approximately $\beta = 0.89$ (dotted black line)

energies, while at lower temperatures, it will minimize the energy towards $U/N = -3$.

We can compare this plot to the progression of the scalar order parameter vs temperature. At the same point

Figure 3: Scalar order parameter as a function of β, again, we notice a phase transition around $\beta = 0.89$

at which we see a sudden decrease in the system energy, we see a sudden, nearly discontinuous increase in the order parameter. As mentioned earlier, for a real liquid crystal system, we would expect a sudden, discontinuous shift from $S = 0$ to $S = 0.6 - 0.9$. We can see approximately this in the outputs produced by our Lebwohl Lasher simulation, with two major caveats - our order parameters is not constant at 0 in the isotropic phase and the transition from isotropic to nematic order is not discontinous. However, as with the energy, this is a byproduct of the finite system size, and thus these results are satisfactory for the simulated lattice.

Another observable quantity that can be used to determine if a phase transition has occurred is the system heat capacity. We calculate heat capacity as:

$$C_v = \frac{(\langle U^2 \rangle - \langle U \rangle^2)}{T^2}$$

This equation, combined with the drastic increase in energy variance around the critical temperature as discussed earlier, should lead to a sharp peak in the heat capacity around $\beta = 0.89$. In our 10x10x10 lattice, we do indeed see this:

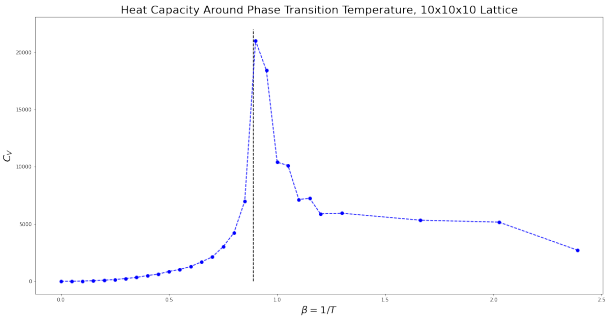

Figure 4: Heat capacity as a function of β, zoomed in to points around the critical temperature. A peak can be observed at approximately $\beta = 0.89$

We can see that, using a standard metropolis algorithm, we were able to recreate the results of the original Lebwohl Lasher paper, as well as supplementary papers on the Heat Capacity and Order Parameter. Simulations near the transition temperature did experience a "critical slowing down", but it was sufficient to just run more equilibration cycles, in the manner of Lebwohl and Lasher. Given my modern computing resources, and relatively efficient python code for the algorithm, I was able to do this in a fairly non-time consuming manner, and produce desirable results. Additionally, runs on a 20x20x20 lattice were run for energy, to see if we could observe any finite-size scaling in the discontinuity of the energy. Graphically, the results produced on this lattice appear virtually the same to those in Figure 3, however, upon closer investigation of the area around the transition temperature, a slight increase in slope could be observed; however, with subsequent runs I could not determine if this was actually the expected finite scaling or just simply some numerical error in the computation of our averages. In the literature, Lebwohl Lasher lattices have been run up to and beyond a 200x200x200 lattice, and according to those

sources, substantial improvements were noted within the observables pulled from the system[?].

5 Wolff Algorithm

As discussed earlier, around the phase transition temperature, the time necessary to equilibrate our system grows dramatically. This "critical slowing down" is a byproduct of our system existing in two phases simultaneously, causing the energy to fluctuate quite dramatically as the system oscillates between the nematic and isotropic phase. Generally, it took about 1000 more lattice passes, which for a 10x10x10 lattice is 1,000,000 metropolis steps, to equilibrate a lattice configuration at or near the critical point. One way to counteract this slowing down is by applying a cluster algorithm. Cluster algorithms, unlike the Metropolis algorithm, rotate multiple lattice points simultaneously as a "cluster" of spins. In our case, we want to look at the Wolff Single Cluster algorithm, which builds a singular cluster of multiple lattice sites and rotates them with the same rotation operator.

The Wolff Cluster algorithm was originally developed by Ulli Wolff for the ising system. In this system, bonds between nearest, spins can only be in states 1 or -1, so the cluster algorithm simply joins parallel spins with a certain probability and flips all of them to the opposite spin configuration[11]. A more general Cluster algorithm was then developed by Wolff, to be applied to lattice systems with a more general spin orientation. Rather than flipping spins, spins are rotated with respect to a vector in the unit sphere, $\hat{r}$, according to the following operator:

$$R(\vec{r}) = \vec{\sigma_x} - 2(\vec{\sigma_x} \cdot \hat{r})\hat{r}$$

Wolff initial algorithm then goes:

1. Choose a random reflection $\hat{r}$
2. Choose a random lattice site as the cluster starter, flip according to the rotation operator and mark it as part of the cluster
3. Visit all nearest neighbors, and link them to the cluster with probability

$$P(\sigma_x, \sigma_y) = 1 - exp(min[0, 2\beta(\hat{r} \cdot \sigma_x)(\hat{r} \cdot \sigma_y)]$$

4. If successful, flip the rotate the neighbor, mark it, and join it to the cluster.
5. Iterate this process until you have exhausted the possible particles for the cluster or until you run out of neighbors to check

Through this algorithm, critical slowing down around the phase transition can be avoided, with the Wolff Algorithm having substantially lower auto-correlation times than the standard metropolis algorithm. Additionally, this algorithm does fulfill the detailed balance conditions, as is proved in the original paper by Wolff[11], and is ergodic, as "There is always a nonvanishing probability that c consists of only one site, and there is always a reflection connecting any two spins. Then each configuration may be reached in principle by at most $|\Lambda|$ update steps"[11]

This algorithm was adapted to work with the Lebwohl Lasher lattice by N. Priezjev and R. Pelcovitz. Their algorithm for the Wolff single cluster method with the Lebwohl Lasher system is very similar to that of the initial algorithm produced by Wolff, with some slight modifications to the rotation operator and probability of cluster formation[8]. It is as follows:

1. Choose a random direction in the unit sphere, $\hat{r}$
2. Reflect any lattice sites for which $\sigma_i \cdot \hat{r} < 0$
3. Then, as with Wolff, choose a random site i and reflect it according to the reflection operator, which is now written as:

$$R(\hat{r}) = -\sigma_i + 2(sigma_i \cdot \hat{r})\hat{r}$$

   Which now keeps the reflected spin in the same "hemisphere" which it started in (we define this Hemisphere with respect to $\hat{r}$)[8]

4. Next, form bonds with the 6 nearest neighbors with the probability:

$$P_{ij} = 1 - exp(min[0, 4\beta(\sigma_i \cdot \hat{r})(\sigma_j \cdot \hat{r})$$
$$\times((\sigma_i \cdot \sigma_j) - (\sigma_i \cdot \hat{r})(\sigma_j \cdot \hat{r}))]$$

   Where $\beta = 3\epsilon/2k_bT$. This probability takes the original probability of the Wolff algorithm and adapts it for the Lebwohl Lasher potential discussed above, which is why β is slightly modified from the standard thermodynamic beta and the probability of forming a bond in the cluster is modified. [11]

5. If a bond is formed, rotate σ_j, mark it, and add it to the cluster
6. Iterate this until no bonds are left to form

Practical implementation of this algorithm necessitates the use of three lists: a cluster list, a old stack list (which includes the lattice indices added to the cluster in the last

run), and a new stack list, which we add the indices of the successful bonds to as we are iterating through the neighbor list. The cluster list makes sure that we do not add the same lattice site twice to our cluster, while the two stack lists make sure we can successfully iterate through successive neighbor lists while building our cluster[12].

6 Cluster Results

The first thing we want to check with our cluster algorithm is if it produces the expected outputs for our system energy around the discontinuity. For a small trial run with only 2000 iterations of our cluster algorithm per run, we produce the rough outputs seen in figure 6.

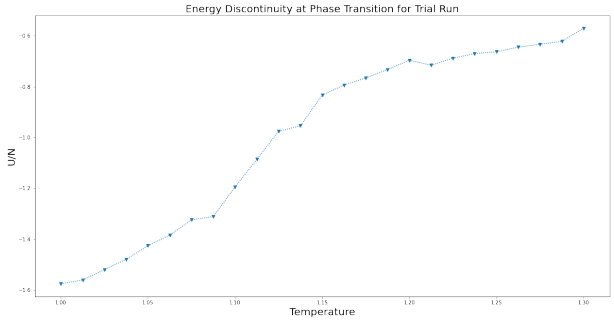

Figure 5: A rough look at the total system energy as a function of temperature. We can see a discontinuity in the system energy at around T=1.1, which matches our expecation from the literature with the Lebwohl Lasher Model

We can see that a discontinuity is present, even at a low number of cluster steps (2000 in this case). For more runnings of our cluster algorithm, we would expect an even better view of the discontinuity, additionally, a larger range of temperatures would provide more perspective to the discontinuity, but this output is sufficient in its purpose of validating the cluster algorithm.

From here, we would like to look at the cluster sizes for various temperatures. We expect low temperatures to have large clusters on average, flipping most if not all of the spins for a single step, while we expect isotropic temperatures to have a low cluster size, near one in the isotropic phase, as the algorithm should be producing very small clusters. We can see in figures 7, 8 that this appears to be true for T=1 and T=2. Finally, if we look at figure 9, we can see that cluster size does indeed decrease as temperature increases, with all temperatures in the isotropic level having an average cluster size of roughly 1.

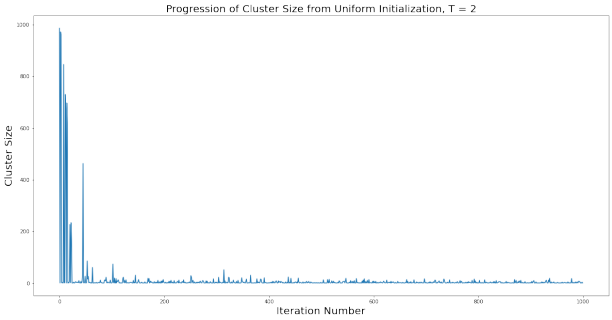

Figure 6: Cluster Size vs Iteration Step, T=2

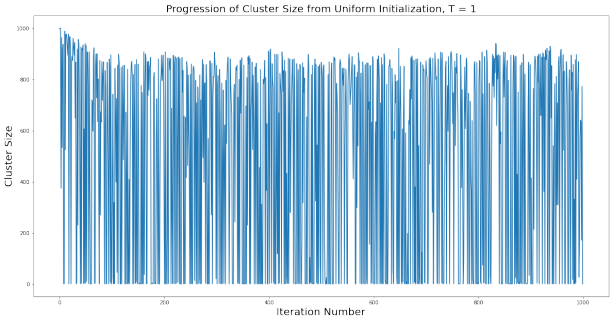

Figure 7: Cluster Size vs Iteration Step, T=1

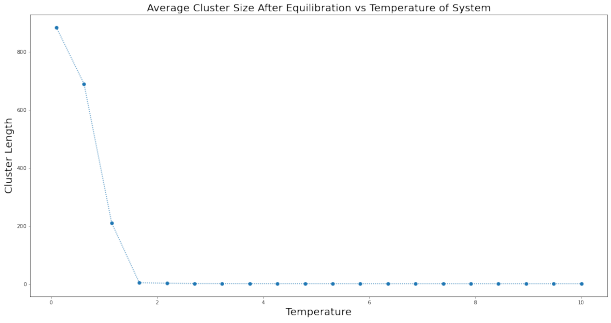

Figure 8: Cluster Size vs Iteration Step, T=1

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