Groundstates of liquid crystals with colloids: a project for undergraduate students.

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Abstract. Although simulated annealing has become a useful tool for optimization of many systems, its initial raison d’etre of achieving the groundstate structure for a spin or atomic/molecular condensed system remains important. Such modelling, whether using analog models such as glass beads or by invoking simple computer models can be suited to undergraduate projects. In this paper we discuss the application of simulated annealing to find the groundstate of a system of liquid crystals (LC) with suspended colloids. These systems are expected to have interesting conductive behaviour, relevant to applications for television and computer screens. In our first stage, a pure LC system was simulated in python and visualized by undergraduates and presented on an educational website. In the next stage colloid(s) were added, and the original code modified accordingly. Interesting effects such as ordering around the colloid have been seen and will be described. In the final stage and in order to study larger samples, the code was rewritten in C++ and several algorithmic modifications were made. Speed up factors between 100 and more than 1000 were obtained, and fascinating closed cells surrounding the colloids were observed.

1. Introduction

This report is part of the Technion Computational Physics Group’s presentation of educational websites with downloadable code on many diverse topics, with special emphasis on Condensed Matter/Statistical Physics topics and model visualization. Earlier presentations \cite{1, 2, 3} cover a wide range of topics. Each project includes physical background, downloadable code and instructions for implementation, and is designed to introduce a topic at a level suitable for other senior undergraduates.

2. Simulated annealing for groundstate search

How do crystals reach their groundstates in nature? The groundstate is the state with the lowest energy, there could be several equivalent ones, or a situation of almost minimum energy which encompasses several domains. Let us consider the example of diamonds, which are naturally formed from molten carbon in high temperature and pressure conditions in volcanoes as they slowly cool or anneal. Rapid cooling or quenching would lead to many small crystal domains. An animated demonstration simulated annealing computer code, using a simple two-dimensional Lennard-Jones (LJ) interaction, between two atoms \(i\) and \(j\), a distance \(r_{ij}\) apart, where \(\sigma\) is the separation of the particles when the potential is zero and \(\epsilon\) is the depth of the potential at its
was presented in [4] to illustrate this. The calculation used simple Metropolis annealing, with a slow lowering of the temperature until an ordered state was found. The code in [4] has an interactive command-line interface which enables dynamic change to the temperature or lowering rate, as well as a visualization window to view the current state. This approach enables the student to self-learn about the optimal cooling rate. A variation for the same model using a master-slave genetic algorithm was given in [5]. For these calculations “reflecting” boundary conditions were used and these will be discussed further below. It should be noted that we are not discussing any behaviour at higher temperatures or phase transitions, (there could be one as the temperature is lowered and the system solidifies) just the groundstate formation and structure. Another model of this type that demonstrates the application of a simulated annealing algorithm is the telescope phasing problem, [6, 7]. These latter models illustrate the importance of scheduling the decrease of “temperature” (noise) appropriately, but we will not discuss this further here.

Another way to educate students about annealing and groundstate search is analog demonstrations [8, 9]. These can be used to demonstrate the annealing process, a full discussion is given in [8] and examples for defects and grain boundaries in [9]. This approach has proved successful for extracurricular work with highschool and young undergraduate students and also as preliminary step for beginning graduate students. It requires a collection of beads or glass balls (such as those used for chemical filters) and transparent boxes. In earlier days one had to use a photocopier to take the images, today a smartphone can be used and so for the present project larger boxes (from empty CD disks Fig. 1) in Figs. 1 were photographed “as is” (Fig. 2), equivalent to a simulated quench then shook to imitate movement as kinetic energy, a simulated anneal and photographed again (Fig. 3). Insight towards a good choice of scheduling can be obtained from the analog systems as well as from discussion of annealing in nature.

The cases, computer and analog, with spherical particles were easy because with spherical particles the domains dissolve with relatively little effort, however once the particles become elongated groundstate search becomes far more difficult. We can take the intuition from the spherical analog systems to the computer to begin our simulations, but we may need additional stages.

Figure 1. The box.  Figure 2. Disorder.  Figure 3. Groundstate.

3. Experimental motivation
The present series of studies began when the Technion RBNI Nanotechnology Institute had a visit by Professor Shunsuke Kobayashi from Japan, who spoke about how colloids could change
the properties of liquid crystals. In discussions following his talk, we decided to begin projects containing educational material with downloadable code to encourage modeling these systems.

4. Visualization and potentials for liquid crystals with or without colloids

Liquid crystal groundstates have long range order in at least one direction, and the molecular objects usually are non-spherical molecules. The Technion Computational Physics/SimPhoNy visualization software, AViz, [10, 11, 12] had a LC option, (proposed by Mike Allen, quite a while ago) that had been used for quadrupole simulations of elongated molecules but never for liquid crystals. (A quadrupole $P_{44}$ ordered state simulated by O. Cohen [13], shown in Fig. 4.) The molecules are shown as cylinders. Within AViz there is the possibility to use color to reinforce the perception of spin direction, and it works equally well on cylinders. As opposed to atoms, that only have a type and location, spins have type, location and a direction with $x, y$ and $z$ components, and can be drawn as pins or cones. The LC option has a location and direction and can have additional properties such as angular deviation from some selected direction, or movement of center from initial location. They can be drawn as lines or cylinders of varying lengths and thicknesses. At this point in time, AViz enables only one type of object (atom/spin/liquid crystal) so the introduction of colloids required a workaround. The colloids are indicated by stars of cylinders joined at the center, which has the added visual advantage over a larger blob of being able to view order thru their branches. However, it is important to note that this is merely a visual trick - in the simulations the particles have the correct spherical or spheriodal shape. A cartoon graph of energy versus configuration space for a simple two dimensional LC system surrounding a colloid is shown in Fig. 5.

A LC potential [14] that has the same general functional form as the LJ was developed by Gay and Berne [GB], for this anisotropic case. Each of parameters $\sigma$, $r_{ij}$ and $\epsilon$ are generalized since there are now orientational degrees of freedom as well as the translational ones and shape anisotropy. There is a wonderful website and educational project about generalised LJ/GB potentials developed by the Concord Consortium [15], which discusses potentials beyond the usual LJ/GB as well as mixed systems. This site is molecular dynamics oriented to study dynamic behaviour rather than groundstate search that is our main concern, but the potentials are, of course, identical. We refer the reader to their excellent exposition for detailed information.

In brief, a unit vector, $\vec{u}_i$, a length $l_i$, breadth $d_i$ and an electric dipole moment $p_i$ are added for each molecule, as well as $\chi$ and $\alpha$ which are functions of the length/breadth ratios. The parameters are now functions of these, with details in [15, 20, 21]. In addition there are

![Figure 4. Quadrupolar order with AViz [13].](image1)

![Figure 5. Cartoon of energy vs. configuration space.](image2)
parameters that can be chosen to include the possible dependence of the well depth and end to end versus side by side values.

There are many excellent research articles concerning liquid crystal simulation and experiment with and without colloids. We refer the interested reader to [16, 17, 18, 19] where more sophisticated methods and models are explored.

5. Groundstates of liquid crystals
The project to present educational sites for liquid crystal groundstate search was begun by Hila Glanz and Izrael Nadir with a python code for the GB potential (including generalization for other potentials) and an interesting webinterface for presenting results as shown in Figs 6 and 7. We used the “color to indicate direction of the molecule feature” of AViz graphics. Each of the screenshots of the interface includes pre-calculated results for the energy and a visualization of the state for selected cases. This project was described in [20]. The present code is also presented on a website [21], where details of the similar and distinct aspects of the two projects are described in depth. Both codes use the same, rather basic simple Metropolis annealing selected for the Lennard Jones potential of [4], but do not have the interactive option since they require much longer run times.

![Figure 6. Screenshot of the interface at high temperature, with AViz [20].](image1)

![Figure 7. Screenshot of the interface at low temperature after annealing.](image2)

6. Groundstates of liquid crystals with colloids
Pure LCs are relatively easy to anneal into groundstates. The addition of colloids complicates this greatly. Some liquid crystals are themselves colloids, but we study the case of small liquid crystal molecules with a few large colloids. Once colloids are introduced, the groundstate structures must satisfy minimal energy of the LCs as well as of their order around the colloids. The first decision is whether one requires the LCs to orient parallel or perpendicular to the colloids. For the 2d simulations parallel was selected, with an intuitive explanation that when you push 1 rod-like object towards a big sphere-like object the rod-like object will try to be parallel in order not to be squashed, all the other rod-like objects are more affected by the rod-like object near them than the sphere-like object which is much further away. The rod-like objects had a rejection between themselves and so tried to fill the space until they reached very close to the colloid. Therefore there was also a rejection between rods and the colloid. The start and end configurations for two dimensional systems with a central colloid are shown in Fig. 8.

In [20] simple periodic boundary conditions were used, since the system was homogeneous. The addition of colloids breaks this symmetry and thus boundary conditions must be re-evaluated. The novel “reflecting” conditions of [4], are not practical or needed here. They were introduced because a simple Lennard-Jones system has a very high vapour pressure and
the default situation with a sample is that the atoms fly away. (This is not the case with low vapour pressure metals [25].) However totally free boundaries can cause problems also with liquid crystals and so periodic boundary conditions were selected. These obviously mean we have a “lattice” of structures and voids, but the structures are at a substantial distance from each other. Despite the differences in models and boundary conditions from [4] the same simple Metropolis annealing is used.

![Figure 8. Screenshot of the interface at low temperature after annealing; rightmost images with different choices of periodic boundary conditions.](image)

Colloids with non-circular shapes were visualized by combining several spheres in rows or squares. This is purely a visualization trick, in the calculations, the true ovoid or circular shapes were used.

7. Further improvements and three dimensional cases
The interactive interface shown in Figs.6 and 7 and Python based coding in [20] have been very useful for demonstration purposes, but three dimensions and colloids took an excessive time to equilibrate.

Thus, in order to proceed further a new C++ code was prepared, validated and then run, with some examples given in Fig. 9. This code is many times more efficient and we are continuing its exploration. Details of the speedup are in Table 1, where the times are averages over all temperatures. Note that in addition to the language change there are also some algorithmic changes and bug fixes in the new code. In the Python code the potential of the whole system was calculated from scratch at each Monte Carlo step! Even if we wanted to calculate the potential of a certain radius, to find this radius we would have had to run through all the molecules to check if they were in the radius. The C++ implementation has a lookup table that saves all the potentials thus we need to calculate only the potentials needed for this change. In addition we added a discretization of the 3d space so we could know in $O(1)$ (on average) the neighbor molecules. The time for one iteration (moving one molecule) is linear in the number of molecules; or to be more accurate $O(1)$ is replaced by $O(m)$, where “$m$” is the number of grid cells that potential covers until it decays. Since “$m$” depends only on the potential parameters we can keep “$m$” fixed and extend the system to contain more and more LC molecules, keeping the iteration time unchanged.

The final structures around the colloids have similarities in 2d and 3d, with circular/spherical symmetries given enough development time. However, in our 3d example we selected an attraction between the colloid and LC and expected and found a “porcupine” structure. The periodic potential and periodic boundary conditions of the LC were already considered in the earlier implementation. In the latest one a periodic potential for the colloids in adjacent systems was added. As expected we found similar results because the system is large relative to the colloid
Table 1. Comparison of times for C++ and Python codes.

| Model               | Steps | Python time | C++ time |
|---------------------|-------|-------------|----------|
| $5 \times 5$ molecules | 100,000 | 21.25 mins | 9.5 secs |
| $5 \times 5 \times 5$ molecules | 200,000 | 3.5 hours | 52 secs |
| $11 \times 11 \times 11$ molecules | 500,000 | 6 days | 8.33 mins |

Figure 9. 3d sample images (l to r) A few steps after initial random state, about 25 percent done, 35 percent, final configuration. The color of the liquid crystal molecules is selected according to their angle to guide the eye.

and the potential of adjacent colloids decays substantially when we look inside our system. The final code can be found on Github [23], and some comments on [21]. We note that for all cases a simple slow temperature reduction has been selected.

One important issue at the level beyond educational codes with simulated annealing when the algorithm is molecular dynamics is the selection of ensemble such that there are minimal constraints on the structural order. This has been studied intensively by Keiko Aoki and we refer the interested reader to her series of papers [22].

Figure 10. An enlargement of the final state shown in Fig. 9 and an analglyphic stereo version [24]. An animation can be found at: http://phycomp.technion.ac.il/~phr7ja/newmovie.gif.
8. Conclusions
This project began as a modest addition to the Technion Computational Physics groups series of educational projects on the simulation of liquid crystals, but was extended beyond the usual scope in order to create large three dimensional models. The structure of the final(?) states in the three dimensional colloid samples as shown in Fig. 10 appears to be very interesting and will be explored further in the future.

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