# Sampling disordered chain configurations in models of organic crystals

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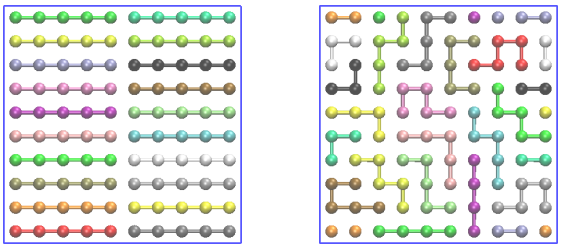
The Physics molecular simulation group is interested in studying the nucleation and growth of model organic solids comprised of flexible molecules. Our research in this area is motivated by a desire to understand crystallisation processes implicated in heart disease and other medical conditions such as gout and kidney stone formation. Of current interest is the model of Polson and Frenkel [3], a minimal model in which molecules are represented by short chains of $N$ soft beads linked with spring-like bonds.

This and related models form close-packed crystal structures in which the beads occupy sites on a regular crystalline lattice. This structure can be realised with a regular array of aligned linear chains, or with links between lattice sites distributed randomly subject to the chain length constraint. This is illustrated with a 2D example in figure 1. The disordered phase can be modelled as a series of short, mutually avoiding random walks. In models where the chains are 'stiff', with an energetic penalty to forming bent conformations, the ordered phase is more stable. In more flexible models, the higher entropy associated with the disordered structure dominates and one expects this to be the thermodynamically preferred phase. In between (the case of most interest) one must perform rigorous calculations to determine the most stable phase, which may be a function of temperature and pressure.

We are therefore interested in algorithms for sampling from the set of disordered configurations available to short chains on lattices. This mini-project will investigate the use of various Monte-Carlo (MC) schemes in this context, with the aim of incorporating a suitable sampling protocol in existing codes (developed within the group) for computing the relative stability of crystalline structures. We will start with the simple system illustrated in figure 1, exploring the efficiency of two MC schemes for unbiased sampling of disordered configurations, before incorporating some energetic preference for linear chains and studying the phase behaviour of the resulting system.

The first MC scheme is based around the concept of double bond re-bridging [1], in which two bonds on neighbouring chains are broken and replaced with two new bonds that link the resulting fragments together. The second uses a generalisation of reptation moves [2]. Here a number of beads are removed from one end of a chain and placed at the other end. As this will lead to overlaps with existing chains, any chains impacted must also be modified, until one forms a closed-loop of reptated chains which preserves



(a) ordered (b) disordered

Figure 1: Two configurations of a fully populated $10\times10$ lattice with chains of length $N = 5$. Boundary conditions are periodic. Bonds which reach across the boundary are not shown.

the required connectivity. Specific project deliverables would include:

- Implementation of the double re-bridging and general reptation algorithms in two dimensions on a square lattice with partial lattice occupancy.
- Example MC simulations at a range of lattice occupancies, measuring behaviour of the two schemes toward the limit of full occupancy.
- Introduction of chain bending energy, and mapping the emergence of the ordered phase.

Should time permit we will consider other lattices and boundary conditions. Computer code developed will feed into an advanced scheme for computing free energy differences between ordered and disordered solids, which in turn will be used to interpret ongoing simulations of crystal nucleation and growth.

A potential PhD project will use these tools to design models in which one can tune the phase preferentially nucleated from the melt, and explore the kinetics of this process with path sampling methods. The project would suit a student interested in computational statistical mechanics and its application to problems in chemical physics. A strong background in computer programming (in any language) would be beneficial.

## References

[1] B. J. Banaszak and J. J. de Pablo. A new double-rebridging technique for linear polyethylene. *J. Chem. Phys.*, 119(4):2456–2462, 2003.

[2] P. H. Nelson, T. A. Hatton, and G. C. Rutledge. General reptation and scaling of 2d athermal polymers on close-packed lattices. *J. Chem. Phys.*, 107(4):1269–1278, 1997.

[3] J. M. Polson and D. Frenkel. Calculation of solid-fluid phase equilibria for systems of chain molecules. *J. Chem. Phys.*, 109(1):318–328, 1998.