Equivalence Class Sampling for Molecular Self-Assembly on Surfaces

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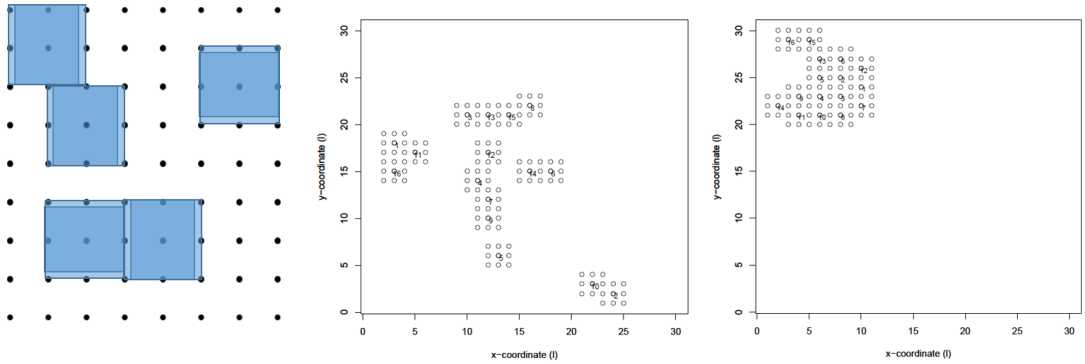
An important problem for materials science is to predict *a priori* what kinds of structures are formed by self-assembly of molecules on metal surfaces. This presentation will introduce a mathematical model for exploring the thermodynamic stability of molecular assemblies on periodic surfaces. This model considers N square blocks on a finite square lattice, each with one of two orientations. The blocks have dimension $2l$ x $2l$, where l is the lattice constant, and the interaction energy between the blocks depends upon their relative alignment and orientation (left-hand figure). This 'block assembly model' captures some key aspects of bottom-up fabrication of graphene nanoribbons from organic precursors on copper and gold surfaces (Han *et al*. *ACS Nano***8**, 2014, 9171).

The block assembly model allows for a rich variety of block assembly structures, and predicting which ones dominate at equilibrium ('optimising' the model) is a difficult problem. In particular, naïve application of typical Monte Carlo methods fail spectacularly, as the blocks quickly gather into a large number of small, mildly stable assemblies and do not adopt other configurations on the simulation time-scale (middle figure). We are developing a new technique called 'equivalence class sampling' for optimising the block assembly model at equilibrium. Equivalence class sampling makes use of the fact that a very large number of the block configurations can be made equivalent by simply rotating the block assemblies and translating them about the lattice. Instead of considering every possible block configuration, we can therefore consider the relatively small number of configuration 'classes', without losing any information on the problem. This affords a major improvement in the efficiency of optimising the block assembly model, however there is a price: equivalence class sampling algorithms turn out to be difficult to set-up. We are developing an algorithm called 'reduction-extension', and early calculations show rapid convergence to very large, thermodynamically stable island structures (right-hand figure).



Left: Sketch of the block assembly model. The two edge designs on the blocks indicate that the sides of the blocks possess different chemical characteristics.
Middle: State of a typical Monte Carlo sampling algorithm after 10^6 steps.
Right: State of the Equivalence Class sampling algorithm after 7000 steps.

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Fields of Research

Stochastic modeling and Monte Carlo simulation for problems in chemical physics.

Publications

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