Gold nanoparticles on graphene: understanding growth and mobility via kinetic Monte Carlo simulation

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Background

Kinetic Monte Carlo (kMC) simulations are well suited to modelling the growth of clusters and films on surfaces. Elementary processes are defined (e.g. "atom arrives at surface", "atom hops one unit on the surface", "atom sticks permanently to a neighbour") and the simulation proceeds by sequentially choosing random elementary processes with a probability related to their rates. From this simple table of processes and rates, complex behaviour can arise: fractal growth, cluster formation, layer-by-layer crystallisation, etc.

In recent experimental work [Small **7** (2011) 3202] we deposited gold atoms on to chemically modified graphene (CMG) and then imaged the resulting nanoclusters in transmission electron microscopy (TEM). The high electron transparency of the CMG allows high quality TEM images of the cluster array to be rapidly obtained, giving us unprecedented statistical accuracy in determining the island size distribution (ISD). The ISD contains a great deal of information on the elementary processes which occurred during growth: these cannot be observed directly but are vital in refining bottom-up nanostructure production.

A kMC model was developed by Peter Dawson (Complexity summer miniproject) in collaboration with Dr. Paul Mulheran at the University of Strathclyde. From this model we determined that the rather odd *bimodal* ISD observed in TEM for Au-CMG was due to cluster mobility, which appears to switch on when clusters get *bigger* than a certain size s_{crit}, but then decrease in rate as they continue to grow. This behaviour is really unusual and we want to improve on the present simple rule (equations given in the figure).

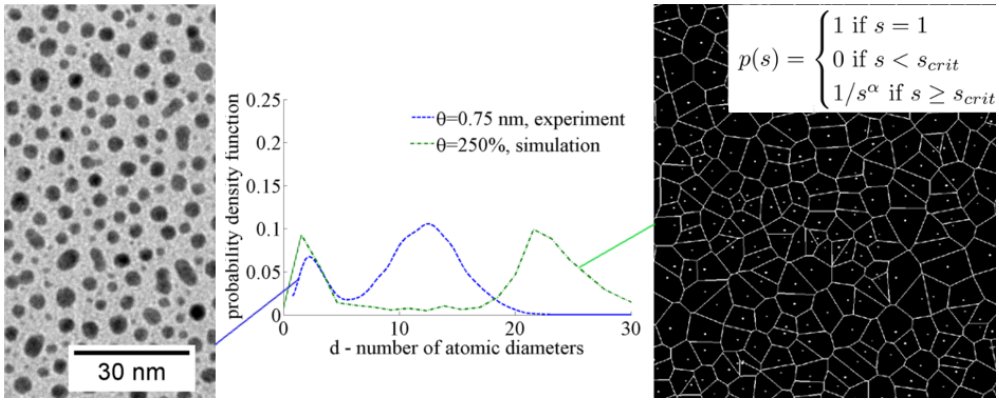

Figure: Experiment (left) and simulation (right) with mobility rule. Between are compared bimodal ISDs for simulation (green) and experiment (blue).

Project objectives

1. Develop a physically justified cluster mobility rule for kMC which *quantitatively* reproduces the experimental bimodal ISDs.
2. Extend the kMC to *structured* migration potentials (e.g. to represent 2-layer vs. 1-layer CMG, or deliberate patterning of the surface by functional groups).
3. Optionally (more likely PhD work) – relate the kMC model to *ab initio* hopping barriers and migration potentials calculated using density functional theory (DFT).

Practical aspects

The student will need to assimilate some background in thin film / cluster growth. The kMC model is implemented in FORTRAN and the project involves tweaking this code, but no "heavy" coding. No new data collection is *required* for the miniproject but we are working on getting TEM data on *in situ* annealing of nanocluster arrays, which will tell us a lot more about the mobility. Modelling this would be great.

Potential PhD work

There is great scope for continuing and extending this work, which would benefit all the graphene research in Physics and Chemistry. Our TEMs and deposition systems will continue to produce state-of-the-art data, so a PhD could focus entirely on modelling (though an interested student could certainly develop their TEM skills and do some actual microscopy). Collaboration with Paul Mulheran on the kMC will continue, and we will also collaborate internally (David Quigley) and externally (Dr. Stanko Tomic, Salford) on combining *ab intio* DFT and kMC modelling for a rigorous approach to the multi-scale problem.