MI-NET Short term scientific mission: Mathematical modelling of nanowire melting

B. J. Florio[1], Host: T. G. Myers[2],

[1]Mathematics Applications Consortium for Science and Industry (MACSI),
Department of Mathematics and Statistics, University of Limerick, Limerick, Ireland

[2]Centre de Recerca Matemàtica, Campus de Bellaterra,
Edifici C, 08193 Bellaterra, Barcelona, Spain

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This scientific mission allowed me to visit the Centre de Recerca Matemàtica for four weeks. For the first week, I was able to participate in the European Study Group with Industry (ESGI) 115. For the subsequent weeks, I collaborated with Prof. Tim Myers on our project, "Mathematical modelling of nanowire melting".

1 ESGI 115

I chose to work on the problem presented by the Inorganic Nanoparticles Group (ING), who are interested in modelling the growth rates of gold nanoparticles in an aqueous solution. At the nanoscale, the surface energy of the particles is not negligible and must be considered when determining the chemical equilibrium of the precipitated nanoparticles and monomer solution. The surface energy is dependent on the degree of curvature which is size-dependent in practise. Thus the solubility of a nanoparticle is determined by its size, with small particles being much more soluble.

To begin the growth process, small nanoparticle seeds are placed into an aqueous monomer solution. Initially, all nanoparticles begin growing in size with the smaller particles growing faster resulting in a monodisperse size distribution. As the monomer is consumed in the process, the bulk concentration will eventually decrease below the solubility level of the smaller particles, which then begin redissolving. The larger particles continue to grow and effectively gain mass at the expense of the smaller particles. This phenomenon is known as Ostwald ripening and has a size defocusing effect on the particle size distribution. Generally, the goal is to produce monodisperse nanoparticles as they will share the same size-dependent properties, so Ostwald ripening is an unwanted effect.

The study group first worked on a model of a single particle which has a size-dependent solubility and found that the process is reaction limited, so diffusion of the monomer can be ignored. After the study group week, this model was then extended to include many particles (in the order of hundreds) and show a clear progression from the initial size-focussing growth stage to the size-defocusing Ostwald ripening stage.

Peculiarly, the ING sometimes do not observe Ostwald ripening which should be guaranteed to occur by the above model. This may be due to the presence of a surfactant in the solution

which coats the particles via Van der Waals forces. The surfactant is used to prevent nanoparticles from colliding with each other and facilitates the precipitation of ionic gold onto the elemental gold particles. The presence of the surfactant thermodynamically complicates the surface phenomena and may change the size-dependent solubility of the particles. We used an analogous model from pharmaceutical literature on emulsions to show that if the particle distribution is initially very monodisperse, then it is possible that Ostwald ripening will not occur.

2 Mathematical modelling of nanowire melting

Nanowires are expected to be at the forefront of the computer and electronics industry. These wires carry an electrical current which will induce an internal temperature rise. At the bulk scale this is usually not a problem due to high melting temperatures, but at the nanoscale the melting temperature decreases drastically and can impede the functionality of the wires. Melting point depression is a phenomenon where the surface energy of the solid-liquid interface is significant enough to alter the thermodynamics of the melting process and causes a change in the equilibrium melting temperature. The physics is completely analogous to the nanoparticle growth problem described above. The degree of melting point depression is dependent on the curvature of the particle and is thus size-dependent.

We use a continuum model to describe the heat flow and melting process of nanowires sitting in a thermal bath with a constant temperature at the outer boundary. At smaller spatial scales, the discreteness of the individual atoms begins to become noticeable, however, it is generally accepted that continuum models in heat problems are accurate for spatial scales down to 2nm. Our results show that nanowires melt slower than nanospheres of the same radius due to the greater surface to volume ratio of the sphere allowing a more rapid absorption of heat. The surface curvature is also greater in a sphere resulting in a lower melting temperature. The melting is a run-away process in that once it begins it becomes easier and easier to melt; as the melting interface proceeds inwards, the melting point is further depressed away from the applied heat at the wire surface.

An analogous solidification problem is also considered. In this case the melting temperature is elevated and we also see a run-away process here. The two problems are almost equivalent except for the fact that the surface energy which is released as the solid-liquid interface proceeds inwards enhances (inhibits) the melting (solidification).

The model is somewhat unrealistic in the sense that the outer boundary is held at a constant temperature and the melting interface begins at the outer boundary and must the held at the size-dependent melting temperature. This results in a situation where the solid-liquid boundary initially travels infinitely fast – a physical impossibility. We eliminated this singularity by relaxing the outer boundary condition to a Newton cooling condition where the heat transfer coefficient is calculated by the theoretical maximum heat flux.

Research continues into the melting of nanowires which are carrying an electrical current. Preliminary modelling indicates that as the radius of the wires gets smaller there is a shift from the bulk-like behaviour where the wire begins to melt internally to nanoscale behaviour where the wire begins to melt externally due to melting point depression.

Results from this research will be presented at the European Consortium for Mathematics in Industry conference, 2016 and at Nanomath 2016. A paper will be submitted to the Journal of Nanoparticle Research within the next month.