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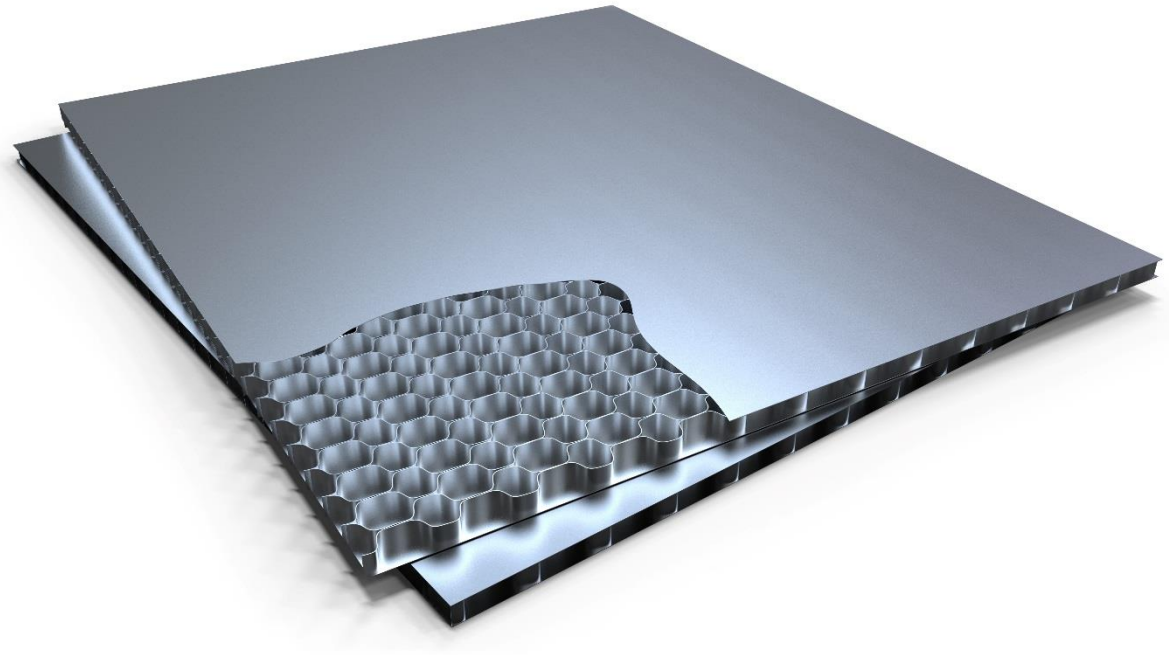

Prediction of Bulk Properties from Microstructure

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1. Introduction

Composites comprise two or more constituent materials

A composite material is one comprising two or more constituent materials. Composite materials are all around us – the concrete that holds up our buildings, the milk we drink for breakfast, the fibreglass surfboards we see (and maybe use) on holiday, and even the wood in the trees growing in the garden and used to construct our tables, chairs and doors. In figure 1 we show the cross-sections of different materials that have been embedded with fibres of glass to form composites. These fibres form complex microstructures which will be a crucial governing factor in the bulk material properties.

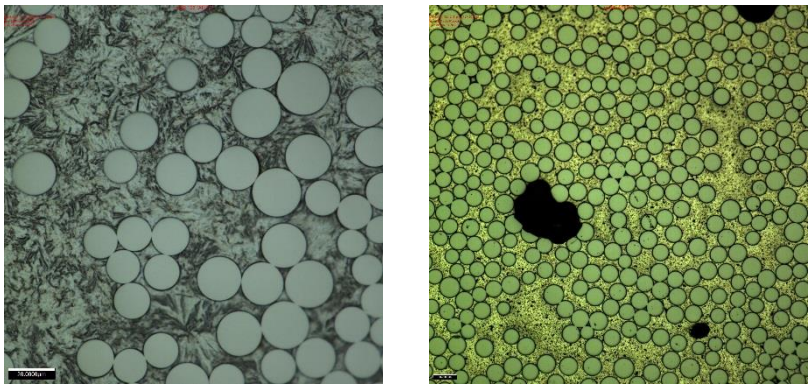

Figure 1: The cross sections of two composite materials. They comprise some background material into which glass fibres, seen as circles, have been embedded. On the right-hand side we see black regions where undesirable voids have appeared from the manufacturing process. The scales in the bottom left-hand corner of each image show widths of 20μ (or 0.02mm). These fibres are approximately ten times thinner than the width of an average human hair (100μ).

There is an increasing demand for models that can capture the mechanical, electromagnetic, and thermal properties of inhomogeneous materials from such complex microstructures, as well as characterise the effects of processes such as wear, corrosion and damage. This is the core activity of NPL's Materials team. There are three main forces driving this demand.

The first is the increasing use of nanoscale reinforcements to design materials with desirable properties. Carbon-fibre reinforced plastics have long been used in applications where low mass and high strength are required, and it is likely that carbon nanotubes and graphene could enhance strength, electrical conductivity and thermal conductivity in a similar way. In all these cases, materials developers want to understand how the reinforcement microstructure affects the bulk properties so that they can manufacture high quality materials in a cost-effective manner.

The second is the increase in ability to create materials with complex microstructures. A good example is woven composites. These materials use similar base ingredients to traditional fibre-reinforced composites, but weave the fibres into a cloth before adding resin to bind the fibres together. This approach can lead to enhanced toughness, but the link between the weave structure and the macroscale properties is still not well understood. An ability to predict bulk properties from microstructure would enhance the design process and allow us to predict the performance of these materials in real-world situations.

The third is the need to predict the properties of materials that contain or develop voids. Materials in challenging environments, such as undersea pipelines or ducts in power plants, undergo chemical changes during their service lifetime and in many cases develop internal voids that can lead to part failure, which can have catastrophic consequences. An understanding of the effects of the presence of voids supports improved part lifetime estimation and enables suitable maintenance schedules to be developed. In contrast, some materials contain voids developed during their manufacture, an example of growing

importance being additively manufactured materials. These materials are often generated by melting a powder or wire in a highly localised region and allowing it to solidify in an uncontrolled manner. This solidification may produce air bubbles and particulate inclusions, such as dust, within the material. If "printed materials" are to be used in load-bearing or safety-critical applications, it is vital to understand their microstructure and effective properties.

Whether man-made or natural, composite and inhomogeneous materials are ubiquitous and fundamental to the engineering of our vehicles and structures. It is therefore crucial that we have a deep, quantitative understanding of how microstructure dictates bulk material properties.

2. Mathematical Models

Maxwell's approach

Maxwell's approach considers the effect of many isolated inclusions

NPL has previously conducted research into homogenisation methods – understanding the macroscopic properties of materials with a known composite or inhomogeneous microstructure. The results were based on a technique originally developed by Maxwell, published in 1873 and later extended by others. The technique measures the disturbance caused by embedding a single particle into an otherwise homogeneous material. The next step then considers the total disturbance of all the embedded particles, called inclusions, to be a superposition of these individual disturbances. This technique ignores the influence of neighbouring inclusions, and therefore should only work when the inclusions are far apart from one another, that is, when the volume fraction of inclusions is small. We found three papers that quantify the volume fraction limitation of Maxwell's method, they are 12.5%, 25% and 50%. It seems there is no consensus, nor is there even a strict definition of what amount of error constitutes an incorrect value.

Maxwell's method results in a closed-form formula for layered materials as well as fibrous and spherical inclusions that is simple to compute. This simplicity makes it appealing, and our main focus is to investigate when this formula is applicable and accurate.

The method of multiple scales

The method of multiple scales is a modern technique that utilises the separation of scales between the macro- and microstructure to extract bulk material properties as a function of the underlying microstructure and material properties. This technique is considered to be particularly powerful since it takes into account the precise microscale geometry as well as the presence of multiple particles and thus is accurate at all volume fractions. However it too has underlying assumptions that may limit its applications – the most critical assumption typically made is that the microstructure is locally periodic.

We might think that this is a very limiting assumption. In figure 2 (left) we see that replicating a single inclusion on a periodic lattice results in a material which does not capture the disorder shown in figure 1. However, if we place multiple inclusions randomly in our microscale cell, as in figure 2 (right), we see that the macroscale periodic geometry appears to capture similar structure to the real-world examples.

The method of multiple scales is more complicated to derive mathematically and more complicated to solve computationally than Maxwell's approach. Having multiple inclusions placed randomly in the microscale structure means we are sampling from a multitude of possible configurations and must therefore run many simulations in order to be confident that the results are truly representative. A principal motivation of this study is to determine whether the multiple scales approach provides additional accuracy.

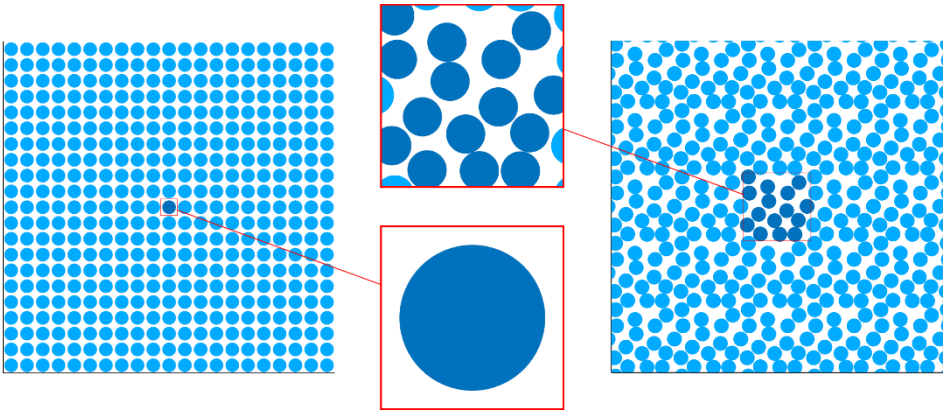

Figure 2: Sample cells and their respective periodic extensions with an inclusion volume fraction of 55%. On the left we extend a cell containing just a single inclusion which makes for a highly structured lattice, whereas on the right we have 15 inclusions in each cell producing a less regular geometry that better models real-world microstructure.

The point inclusion method

We also investigated the point inclusion method. This method takes into account the local geometry and effect of neighbouring inclusions to produce a simple, closed-form formula. However, it assumes a low volume fraction and just like Maxwell it is unclear at what volume fraction this approach is no longer accurate.

A direct numerical simulation

We require a solution to which we can compare these three methods. To this end we carry out a direct numerical simulation of a test problem. We use a test case of thermal conductivity, in which we represent a wire of the composite material as a long array of many identical inclusions embedded in the surrounding material. We thermally insulate the length of the wire, keep the ends at a constant temperature, and consider some heat source acting on the whole material. We then find the thermal conductivity (of a homogeneous material) that, under the same conditions, produces a temperature profile best matching the simulated results.

Glossary of terms

- Inclusion: An inclusion is a material embedded in a surrounding material. This can be a ply in a layered composite, a fibre or a small particle.
- Volume fraction: The volume of a constituent material divided by the volume of all other material. A volume fraction close to zero means there is relatively little of the constituent material, whilst a high volume fraction, that is, closer to one, means there is a relatively large amount of constituent.
- Microstructure: Small-scale structure of a material. Composites often possess a well-understood microstructure, like the glass fibres in figure 1.
- Effective properties: Material properties of the inhomogeneous or composite material on the macroscale.
- Relative error: The error of a measurement divided by the value from the direct numerical simulation.

Heat transfer occurs at a higher rate across materials of higher thermal conductivity

3. Results and Discussion

We use the three methods to calculate effective thermal conductivities and compare these with the result from our direct numerical simulation.

The ordered square lattice

We first consider spherical inclusions in a square lattice and we calculate the effective thermal conductivity, k_{eff}, given the ratio of the thermal conductivity of the inclusions and the surrounding material, k_p/k_m. We show the results in figure 3 for several values of the thermal conductivity ratio over the applicable range of volume fractions, denoted ϕ. The volume fraction is bounded above by the critical packing density, that is, the volume fraction where all the spheres touch.

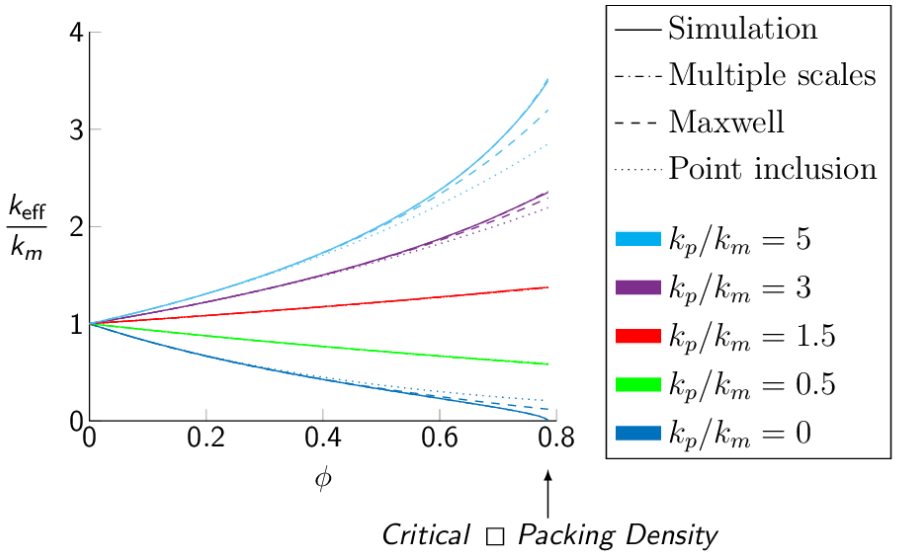

Figure 3: The effective thermal conductivity, κ_{eff}, as computed by all three methods for thermal conductivity ratios k_p/k_m, at various volume fractions ϕ, in the square-lattice configuration (as in the left-hand side of figure 2). The highest volume fraction attainable is indicated as the critical square packing density.

We find that the multiple scales results match almost perfectly with the direct numerical simulation and the lines are indistinguishable. The results for Maxwell's method and point inclusion are good at low volume fraction; the agreement gets worse as we approach the critical packing density, or where the conductivity ratio is near unity.

We set out to produce a more quantified measure of the accuracy of Maxwell's method. In order to do so we consider the signed relative error between Maxwell's method and the direct numerical simulation, for a wide variety of inclusion conductivities and at all the available volume fractions. The sign indicates whether the error is an overestimate or an underestimate. A signed relative error of 1 means the approximation has overestimated by 100% of the "real" value, whilst a signed relative error of -1 means the approximation has underestimated by 100%. These results are plotted in figure 4. Whiter regions indicate areas of low relative error where Maxwell's method is more accurate. The more red or blue the colouring the greater the relative error; red is an overestimate, blue an underestimate.

Maxwell's method is accurate at low volume fractions or for inclusions of conductivity close to the surrounding material

From figure 4 we see that for the square-lattice configuration Maxwell's method is indeed accurate at low volume fractions as well as cases where the inclusions have a conductivity similar to the material into which they are embedded. For high volume fractions and inclusions with thermal conductivity significantly different from that of the surrounding material the approximation is less accurate.

Disordered random configurations

The ordered configuration, as in figure 2 (left), provides a good demonstration of the power of the multiple scales method as well as a good indicator of where Maxwell's method and point inclusion fall short. However as noted, we are looking to provide a concrete quantification of the accuracy of these methods for real-world, disordered

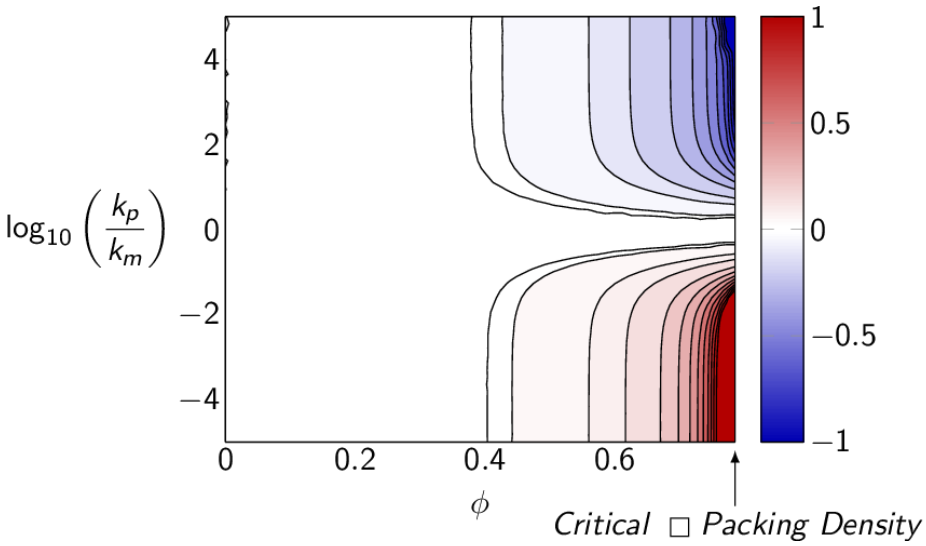

Figure 4: The relative error of Maxwell's approximation of thermal conductivity when compared to the ground truth calculation, for various thermal conductivity ratios k_p/k_m, at various volume fractions ϕ, in the square-lattice configuration. The highest volume fraction attainable is indicated as the critical square packing density.

microstructures as in figure 2 (right). In this disordered scenario a full-scale simulation is significantly more computationally expensive, and performing a sufficient number of such simulations so as to be statistically significant was infeasible. Therefore in this case we compare Maxwell's method to the multiple scales calculations averaged over many realisations of the random configurations. Our work on ordered lattices suggests that this is an excellent approximation for the effective thermal conductivity of the material. In figure 5 we show the relative difference between the results obtained using Maxwell's method and the multiple scales method averaged over 500 realisations.

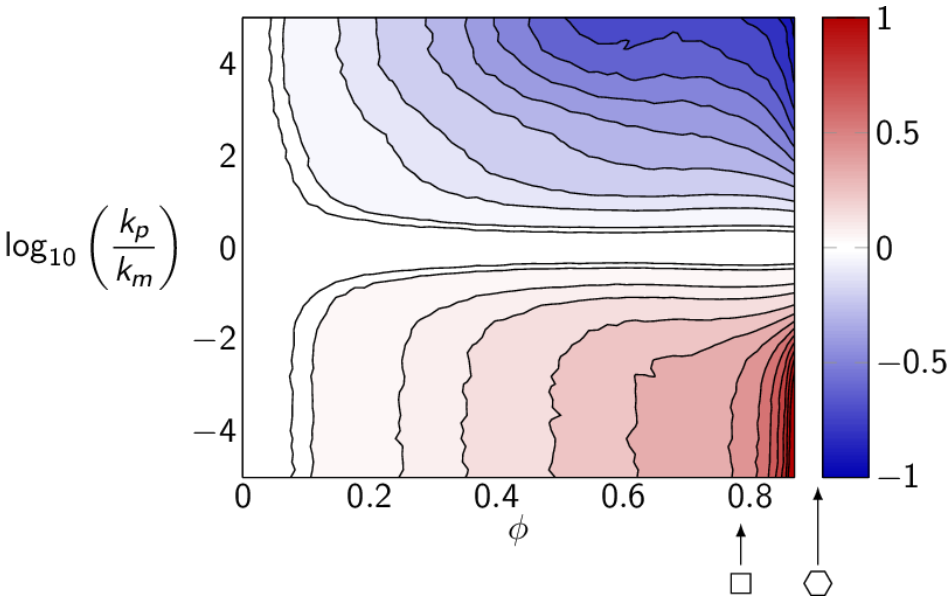

Figure 5: The relative difference between Maxwell's approximation and the average of 500 multiple scales simulations with random configurations of 15 inclusions in a cell extended periodically (as in the right-hand side of figure 2) for various thermal conductivity ratios k_p/k_m, at various volume fractions ϕ. The highest volume fraction attainable in the square-lattice configuration is indicated with a square, and the highest volume fraction attainable in any planar configuration is indicated with a hexagon and just exceeds the range of volume fractions simulated.

We note that the shape of the contours is similar to those of the square-lattice configuration from figure 4. Here however the coloured regions cover more of the plot, which means that Maxwell's method is less accurate than in the square lattice case. This is because the square lattice separates the inclusions well and therefore Maxwell's assumption that the inclusions are well-separated from one another is more accurate. However in real-world configurations, as simulated here by random geometries, even at low volume fractions we already observe particles that lie close to one another. Multiple scales is able to take these geometries and the effect of closely positioned particles into consideration, whilst Maxwell's approximation is not.

Returning to one of our original aims: Our work provides a framework in which to quantify precisely how inaccurate Maxwell's method is for each volume fraction and conductivity ratio.

Future work

The simulations focused solely on thermal conductivity however this is equivalent to many other physical properties, for example electrical conductivity and antiplane shear. Moreover the same techniques can be used to derive other effective properties and the results and conclusions drawn in this study should provide insight into the accuracy and applicability of the methods in general.

The simulations presented are only for two dimensional configurations modelling fibre reinforcements. The same approach can be extended to three dimensions for particle reinforcements.

4. Potential Impact

Many of the measurement techniques that NPL use were developed for homogeneous materials. In many cases, these methods can be used with inhomogeneous materials, but the techniques cannot provide the predictive ability to enable materials manufacturers to develop new recipes. NPL believes that materials measurement for high-value manufacturing needs an understanding of how microstructure affects performance, derived from a combination of multiscale measurement techniques, imaging methods to characterise the microstructure, and modelling tools to predict bulk performance from measurements and images.

Louise Wright, Principal Research Scientist at NPL commented:

In the short term, this work will feed into NPL's project on linking images, measurements and bulk properties. This work that has been done has given NPL some understanding of the limits of our current techniques, and acts as a valuable introduction to the multiple scales method. It is unlikely that we would have considered the multiple scales method without the input from Oxford.

NPL plans on extending this work by analysing a real material using the various techniques available to us and validating our predictions against bulk-scale measurements. The intended impact of this work is two-fold: the knowledge that we gain from our comparison of methods will be disseminated to materials designers as guidance on the strengths and weaknesses of the methods, and the case study showcasing our imaging, measurement and modelling capability will be used to seek future collaborations and third-party business with designers and manufacturers.

In the longer term, this work will support establishment of a measurement service for characterisation and analysis of materials whose microstructure governs their behaviour. This work could also support an inverse approach where the properties of the component parts of composite materials are estimated based on measurements of bulk-scale properties. This service would benefit manufacturers who may lack information about the components they use, and it would support characterisation in cases where the properties of the components are changed during the manufacturing process, for example where the manufacturing process leads to a reaction between materials leading to altered properties.