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SELECTION OF THE EDITOR

Not too big, not too small: The appropriate scale

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The tools we use at the human scale, whether mechanical, medical or microelectronic, depend on materials for which some other scale of length or time is critical. Often this is the mesoscale, between the scales of engineering and of atomic science. Linking underlying processes to what we handle is sometimes called ‘spanning’ (or ‘bridging’) length scales, giving the impression that the mesoscale is a swamp to be crossed without getting mud on our boots. This is misleading: we do not wish to span the mesoscale, but to work at the appropriate scale, and to connect that to our human needs. The appropriate scale need not rule out multiscale computer modelling, in which some supercode integrates relevant scales in one pass, hoping to combine the best of methods for two or more levels. But the reality for such attempts, too often, is that the worst of both regimes are found. Happily, simpler strategies at a judicious scale will often suffice.

WHAT IS MESOSCOPIC MODELLING?

Pick up a piece of steel or ceramic. Examine it with increasing magnification, from the naked eye to the atomic force microscope. It will show a hierarchy of natural scales. There is roughness which can be felt without tools (the ‘thumbnail test’). Grain structures are observed, with dislocations, and inclusions of other phases. Then come space-charge regions, or atmospheres of impurities around dislocations or segregated to interfaces. Finally, atomic structures come into view. Mesoscopic features are those with characteristic scales between the atomic and macroscopic, and can be crucial in how materials perform.

In state-of-the-art microelectronics devices, some structures will have a natural scale. Other, operational, scales will be determined by compatibility with previous generations of devices, or by the laws of physics and the art of the possible. Sizes are chosen to optimize signal speed and memory stability, and to minimize energy dissipation. Research-level devices go further: feature sizes may be fixed by optical wavelengths (photonic devices), electron mean free paths, tunnelling lengths and perhaps quantum coherence. The challenge is control on the operational scale.

For biological systems, operational scales have evolved to match the natural scales. A hierarchy of

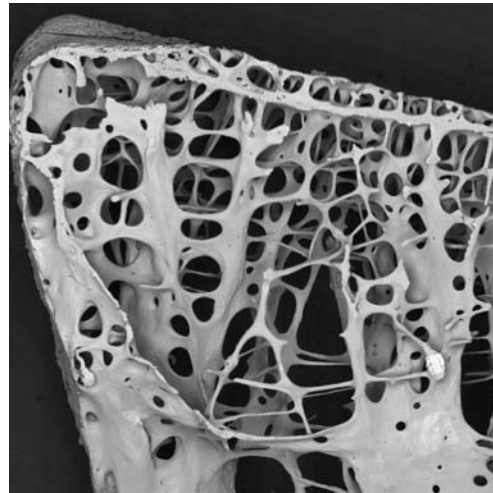


Figure 1 – Bone is a hierarchical material which is also a self-designing system. The picture shows the architecture of cancellous (spongy) bone. The struts (trabeculae) can adapt to the applied stresses on the system, thickening along lines of greatest stress. (Scanning electron micrograph of bone of 75-year-old male, 8x magnification, field width 11mm x 11mm, courtesy of A. Boyde, Dept. of Anatomy, Univ. College, London.

scales is often seen. In the spongy (cancellous or trabecular) variety of mature adult lamellar bone, the interconnected bars (trabeculae) and plates of bony tissue can be resized and reshaped by osteoclasts (bone-destroying cells) and osteoblasts (bone-forming cells). At the micrometre scale,

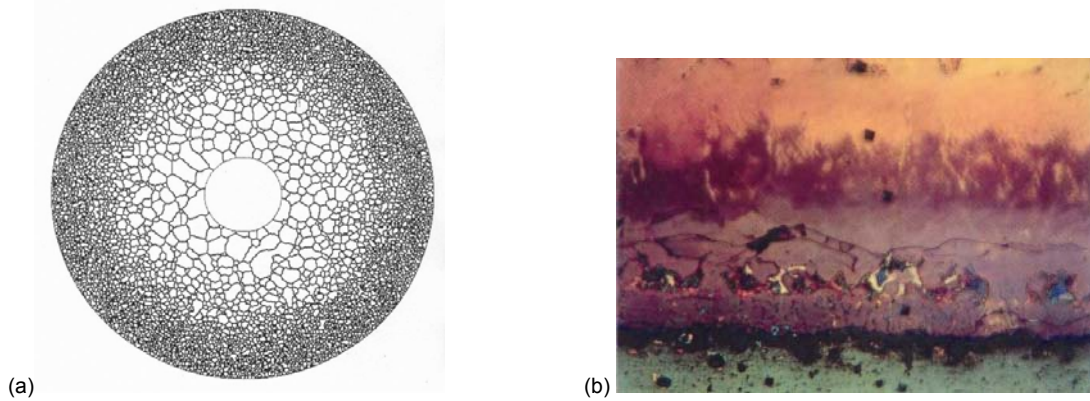


Figure 2 – Grain structure in a nuclear fuel element. (a) Structure calculated²⁷ using a Potts model, showing the substantial effects of grain growth in the hotter central regions. (b) Optical micrograph of cross-sections through Zircaloy-4 in contact with pure uranium dioxide after heating for 12 hours at 10,000°C.

there is a ‘plywood structure of layers (lamellae) of ~3 μm bundles of collagen fibres. Bone salt crystals (impure carbonate apatite) fill much of the water space in the collagenous matrix¹. This hierarchical structure is shown in Fig. 1.

Natural systems demonstrate important issues. First, how well need a structure be controlled? In biological systems, small molecules are exact. Larger molecules (such as DNA) are exact where it matters. Proteins fold precisely enough, and that is no mean feat. ‘Good enough’ can mean brilliant for a specific purpose, but without adaptability, or it can mean optimal given the starting point. The panda’s ‘thumb’ is not optimal as a thumb, but may be the best compromise, if indeed pandas evolved from omnivorous carnivores (like bears), where the ‘true thumb’ forms part of the foot pad². Second, how much is planned and how much can develop? The brain connects in ways for which there are guidelines, not the rigid plan of a silicon microcircuit. The largest biological systems allow

great diversity within recognizable formats, for example in visual appearance. Third, natural systems, like the brain or its neural-net mimics, can learn. They are self-organized in the important sense of adapting to external events, defects or unplanned constraints. The ability to learn means that history-dependence is not a problem for natural systems. History-dependence has to be accepted as a component of materials optimization.

The idea of an appropriate scale for a given system and property emerges repeatedly. There might be several such scales, depending on the property. For a tree trunk, the appropriate scale for strength differs from the appropriate scale for water transport. For photochromic sunglasses, the scale for metal colloids contributing to darkening is much less than that for mechanical robustness. Identifying the right operational scales is a first step on the way to optimizing mesostructures by guiding a system to adopt the right scale.

Engineering modelling uses established methods: finite elements, finite differences, computational fluid dynamics. Atomistic modelling of materials is widespread, albeit with gaps and variable accuracy. Connecting the physics, chemistry and engineering of these several scales³ means addressing the mesostructure somehow. Box 1 identifies some of the approaches and issues in making this connection. Understanding mesostructure is already accepted in optimizing mechanical properties. Early ideas by Cottrell⁴ and others underpinned dislocation engineering, making possible the remarkably efficient use of materials in the modern beverage can. For fluids at the mesoscale, issues might be competition between viscosity and inertia, or polydispersity in colloidal systems. The mesoscopic modelling of functional materials offers great opportunities to improve

Box 1:
APPROACHES AND ISSUES IN MESOSCOPIC MODELLING

Class of theory	Approach	Issues
Bottom-up (more and more atoms)	Order-N methods Massive molecular dynamics	Still not big enough for key properties. Convergence on the right answer not assured. Length scales may be reached, but timescales usually hopeless. May give numbers, but this does not guarantee understanding.
Rational scale	Polymer strand array Colloid Dislocation array Particle dynamics, in which the particles are not atoms	How do you define the properties of the basic components?
Top-down (adjust continuum theory to correct the most serious approximations, such as elastic anisotropy, as necessary)	Finite element Finite difference Fluid dynamics	The adjustments depend on the system and may be history-dependent; examples in hydrodynamic dispersion and turbulence modelling. Also problems with using Navier–Stokes equation in microfluidics. Phase separation and size segregation found in polydisperse systems.

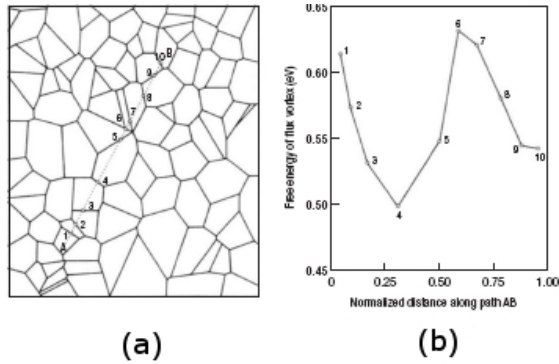


Figure 3 – Variation in flux line energy in a ceramic superconductor. (a) Grain structure predicted by growing grains from random initial nuclei. (b) The free energy of a flux vortex calculated at each of the positions 1-10 marked along the line in (a). The variations in free energy, of the order of 0.1eV, are a measure of the resistance of the microstructure to (thermally activated) flux motion. The grain boundaries are assumed to be Josephson junctions. The differences in superconducting phase (Ginzberg-Landau order parameter) across the boundaries are an important component⁴².

performance in, for instance, medical materials and minimally invasive dentistry. For safety-critical systems, the value of mesoscopic modelling has been shown in the nuclear fuel modelling that guided the running of the Prototype Fast Reactor in the 1970s and 1980s, and made possible retrospective understanding of what went wrong at Chernobyl.

In exploiting mesoscopic modelling, it is crucial to understand what determines behaviour. Merely constructing a credible image of a mesostructure is not enough. Early simulations of columnar film growth using ballistic models correctly predicted the relationship between the angle of growth of the columns and the angle of incidence of the incoming particles, yet the length scale of the pore structure was completely wrong⁵⁻⁷.

CONSTRUCTING A MODEL MESOSTRUCTURE

An optical microscope can show grain structures in a typical ceramic. To predict how that ceramic will behave, we probably wish to mimic it by creating realizations of the microstructure. How should we do this? Will the mimics be good enough for our needs? Our realizations must both look like the system we model and behave as that system does. Some approaches take an image and use it directly in a model, for example to show how specific features would affect surface roughening during laser ablation⁸. Careful analyses of the visible and measurable features of the

structure^{9,10} identify subtle but significant features. A considerable problem is how to use information from a two-dimensional image to recreate a three-dimensional microstructure. Linking a 3D system to the 2D image of the mesostructure can be ambiguous. The first attempts¹¹ imposed major assumptions on the shape and distribution of embedded objects. Methods based on the disector principle now permit unbiased sampling (see ref.12 for a general introduction to stereology), and recent technological developments (X-ray microdiffraction, microtomography^{13,14} and confocal laser microscopy^{15,16}) are important in obtaining three-dimensional images of microstructures. These new developments will allow proper validation of model microstructures.

A second important class of approach mimics the processes that led to the real microstructure. Among the many approaches are rate theory, classical nucleation theory and various direct simulations using kinetic Monte Carlo methods^{17,18}. For growth of films and clusters, simple models include solid-on-solid methods, DDA (deposition, diffusion, aggregation) and DLA (diffusion-limited aggregation)¹⁹. For solidification, again there are useful models²⁰⁻²², including those based on cellular automata. For foams, models may be based on ideas of packing²³. More complex models use statistical methods—for example, the Potts model²⁴⁻²⁶ as a route to grain structures in which interfacial energies are central; Fig. 2 shows an example²⁷, together with an even more complex real interfacial microstructure.

Whichever approach is chosen, the key question is how it is to be checked. Visual appearance is not enough. Even though fractals make possible good computer images of complex landscapes, they have limited promise for model mesostructures. Partly this is because fractals have no intrinsic scale length, whereas all mesostructures involve characteristic lengths. Claimed fractal trends rarely hold over more than two orders of magnitude. Even the broader trends identified (trends of surface roughness²⁸, for example) can only be obtained as an ensemble of much shorter ranges. Hierarchical systems, an important class, cannot be self-similar. Analyses²⁹ of fractal dimensions for morphologies of a range of systems³⁰ show no special correlation of morphology with fractal dimension. If a fractal method is to be really useful for surfaces, it should go beyond topography to give a consistent description of tribology, of ultrasonic and optical scatter, of thermal and electrical resistance, and of other quantifiable properties.

CHALLENGES AND STRATEGIES

Behaviour at the mesoscopic scale determines widely varying phenomena. One simple description of applied materials classes them as structural or functional. Structural materials are exploited for their mechanical properties. Functional materials have some other purpose, perhaps using electrical, thermal or optical properties. Obviously, some materials may have several functions. Ice-cream, for example, needs more than taste and colour. It needs the right texture and thermal properties, controlled by the proportions of fat globules, air bubbles, ice crystals and continuous serum phase. The manufacturing process controls 'mouthfeel' in a complex way³¹, and certainly through the size distribution of ice crystals³²⁻³⁴. Simple mean-field models have some practical use but cannot predict size distributions³⁵. Some biological materials such as wood can be both structural (holding the tree up) and functional (pumping water up to the leaves), with different scales for these different roles.

A second important characteristic is whether the property of interest is an average property of the system, or is a property that depends strongly on special rare features, such as sites initiating electrical breakdown.

For an average property—an elastic constant, for instance—one might use an effective medium theory or perhaps average out some timescale. When rare features are crucial, as microcracks are for fracture initiation, one must construct many realizations of a mesostructure. This is often the case; examples include fracture, electrical breakdown in gate dielectrics, the superconducting critical current in an oxide ceramic superconductor, plastic behaviour of diamond-like carbons, efficient operation of organic luminescent diodes, and the laser ablation of structured ceramics, including teeth. The rare features will have characteristic statistics. If we need many realizations, it is not sufficient to get a morphology right. We have to get good statistical descriptions of other properties. These might be local properties, such as Josephson junction properties or intergranular fracture energies, or non-local properties, which describe the indirect effects of changes nearby, such as load redistribution when one link fails, or magnetic field changes when one grain goes superconducting. Normal statistics do not apply. Often, a weakest-link model is used as a statistical guide. Even for the common Weibull model^{36,37}, parameterization can be very inexact. Moreover, the Weibull model

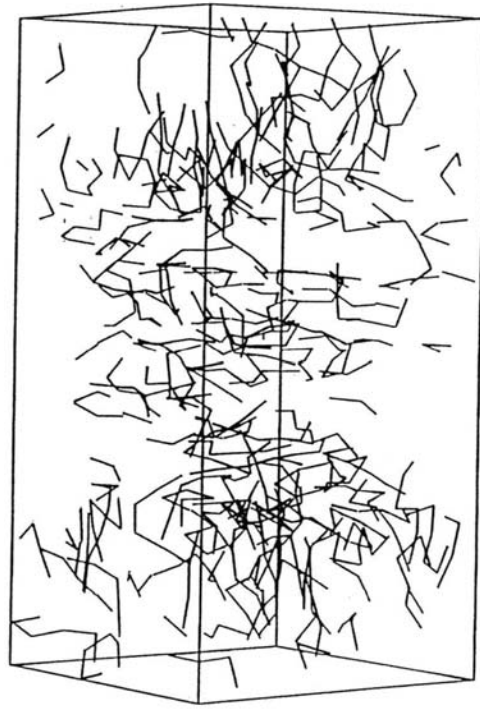


Figure 4 – Model polymer structure for a light-emitting diode. This is a possible optimum mesostructure where chains in the outer transport layers are orientated perpendicular to the electrodes to ensure efficient transport of the charge carriers away from the electrodes at the top and bottom of this image. The central emission layer consists of chains aligned parallel to the electrode plates to cause accumulation of space charge for an increased rate of recombination. Structures such as this have been used by Stoneman and Ramos^{49,50}.

is only one simple example of a much more general class of extremal statistics^{38,39}. 'Self-organized criticality' is very closely linked to the extremal statistics of systems which are controlled by non-local properties. It is easy to produce simple models that show extremal behaviour. It remains very hard to match quantitatively the extremal behaviour of a real system in any non-empirical model.

Other factors may influence a choice of approach. The appropriate scale could involve both time and length. There may be an externally controlled time, such as a heating time. There can be a ballistic process: the time a molten ceramic drop takes from plasma heating before splatting onto a substrate, or the time for electron transit across a mesoscopic conductor. The characteristic time t might be related to a length L by a characteristic velocity, for example L/c when c , the velocity of light, is involved. If there are diffusive processes, whether of heat or atoms, the characteristic time t and distance L are related by $L^2 \sim Dt$ for constant diffusion constant D .

Of course, D may change with mesostructure, increasing as grain boundary diffusion becomes more important.

These various time dependences can be intimately mixed. In nanotechnology, there is a scale defined by how close two components can be before they interfere with each other, whether through tunnelling or electrostatics. This constrains operation at particular frequencies. In film growth, different regimes are defined by the rate of arrival relative to the diffusion time^{17,40}. Whether voids in nuclear material grow randomly, or as an ordered array, depends sensitively on the balance between several rates⁴¹. Processing timescales must be linked to natural timescales. When the system is time- or history-dependent (examples are nuclear fuel elements through their life cycle, or the way bone develops), processes can be hierarchical. In nuclear reactor steels, the nature of copper precipitates (formed in a few picoseconds in a collision cascade) determines embrittlement and whether a reactor can operate for an extra 10 years. In laser ablation, those electrons excited early on absorb energy and change what happens later.

Further special issues may need to be addressed. First, is coherence involved? Coherence can take several forms. How long is an electron mean free path relative to the dimensions of a conducting element? Is the phase

of a superconducting wavefunction important? For vibrational coherence, does a single-frequency mode dominate? How strong is dissipation? Is there quantum coherence (entanglement and its loss, essentially quantum dissipation)? Second, is ordering important? Self-organization is only one of very many examples. If there is ordering, what determines the scale length? Is it kinetics, energetics or some hidden structure? Random features can develop even in models based on regular grids, such as models of flux vortices in superconductors. Microstructure-related features determine energy contours for superconductor flux lines (Fig. 3)⁴² and hence the performance of ceramic superconductors.

CAN YOU CHECK YOUR MODEL?

Judging the quality of a mesoscopic model is a serious problem, especially when there are several length scales. It is not enough to combine state-of-the-art atomistic theory (which is not always right) with a mesostructure checked only by eye. A good rule is always to check an approach against measurements of similar properties. Thus fracture predictions should be tested against fracture data. How the mesostructure is monitored matters as well: measurements should reflect the features that matter. Textural 'feel' and heat transfer in ice cream are critical to customers, but not easy to measure with usual materials

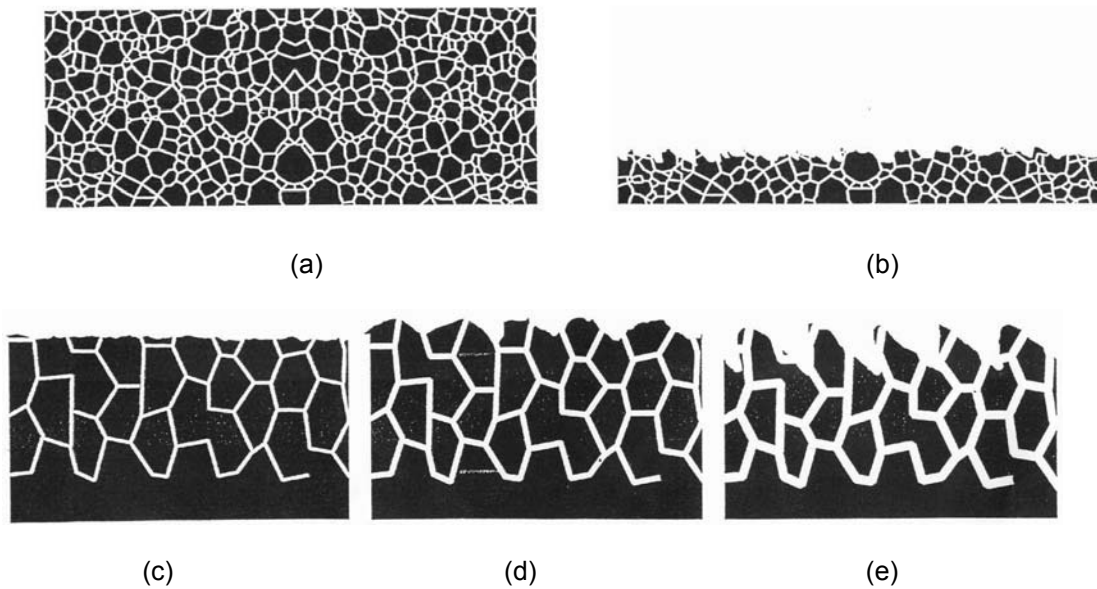


Figure 5 – Surface evolution during laser ablation of a ceramic. The initial grain structure is taken from a 2D experimental image (a), which evolves with time as predicted by Monte Carlo methods (b). Images (c)-(e) compare the evolution for grain boundaries of different widths. For the widest grain boundaries (e) ablation is most rapid, and shows the characteristic cones pointing along the direction of the incident particles.

science methods. Much of the relevant literature⁴³⁻⁴⁵ relates to structural materials. For this reason, our examples relate to functional materials, which are even more varied and less often discussed.

Ideally, predictions for the mesoscale should lead to what can reasonably be measured. It may be prediction of a property, or a bound on properties, or a distribution of properties. It might identify unexpected features, or link results on a complex system from different experiments, such as radiation effects on flux exclusion, magnetization, surface resistance and normal superconductor transition characteristics for a ceramic superconductor. It could define a route to a given performance, or the optimization of a process to obtain a particular mesostructure. Simply 'looking right' without quantification is inadequate.

ORGANIC LIGHT-EMITTING DIODES

Our first example concerns texture in organic light-emitting diodes. A polymeric semiconductor is not just like silicon with altered materials parameters (bandgap, effective mass). The polymeric texture (what one might describe as 'spaghetti structure') introduces local anisotropy and inhomogeneity, because the polymer strands can have various lengths and be aligned, curved, twisted and cross-linked. Figure 4 shows a realization of a 'spaghetti structure' for a possible light-emitting diode, in which random features are subject to chosen statistical guidelines. The importance of texture is long established for polymer mechanical properties and insulating polymers, and is observed for devices such as light-emitting diodes⁴⁶⁻⁴⁸. Model mesostructures can be used in Monte Carlo calculations^{49,50} to evaluate effects of chosen textures on the relative proportions of radiative recombination and of losses through nonradiative processes or ohmic conduction, or simply to assess the value of additives. This can be done by integrating models at the atomistic (electronic), mesoscopic and macroscopic levels. One counterintuitive result emerges from the discreteness of space charge and the complex molecular geometries consistent with the texture. Even when there are no traps (all molecules have the same electron affinity) there can be significant 'trapping', with charge localized on a single strand for a time long compared with the typical transit time through the device. This behaviour is similar to that inferred from experiment as the 'Coulomb glass'.

LASER ABLATION OF CERAMICS

A second example concerns the laser ablation of ceramics, in which an intense laser beam removes material from a solid surface. The aim might be to shape the surface, or to sample the surface for analysis or to deposit material on another surface. Energy is absorbed and redistributed, and energetic surface ions or electrons emitted. The behaviour is hierarchical, because excited electrons can absorb energy, and emitted electrons cause an electric field which tends to pull out positive ionic species⁸. The energy absorption can be highly inhomogeneous. For example, the absorption of subbandgap light by MgO occurs primarily at surfaces or grain boundaries⁵¹, and probably in the impurity or defect atmospheres close to them. After excitation, energy is redistributed, partly by electron motion and recombination. This leads to very high electric fields, especially close to the grain boundaries.

The fields change in time as electrons and ions leave the surface at rates that can be predicted in Monte Carlo simulations of model microstructures. The characteristic manner of surface roughening is shown in Fig. 5. At the surface itself, if the laser beam is not normal to the surface, cone-like structures emerge through the shadowing effects known from ion bombardment⁵². For ceramics such as MgO, the main aims might be accurate machining, and choosing conditions for surface roughening or smoothing. For minimally invasive dentistry using a CO₂ laser, there are different aims. Certainly, one wants removal of bad material and a final surface mesostructure optimized for replacement material. But also one seeks minimal removal of good material, avoidance of thermal shock to the patient, and the survival of the tooth. The energy absorption is inhomogeneous, as for MgO, but for the tooth the absorption is primarily by water in its various forms, whether as liquid or as water of crystallization in apatite structures. The nature of the absorption and the mechanisms of fracture and particle ejection vary with this inhomogeneity. There are strong dependences on mesostructure and hierarchical behaviour which allow optimization of the laser parameters.

THERMAL BARRIER COATINGS

Thermal barrier coatings provide a third example. In an internal combustion engine, these are the thermal insulating coatings between metallic engine components and the hot gases. They must limit heat flow, and also resist spalling and

corrosion. A typical microstructure is shown in Fig. 6 for a plasma-sprayed coating. Such coatings are created by injecting powder particles (a few micrometres in diameter) into a plasma gun. The particles liquefy in the plasma and are hurled against the surface to be coated. They splash, forming thin lamellar splats which pile up to form the coating. The microstructure, notably the nature and distribution of the porosity, determines both the average material properties (thermal conductivity, Young's modulus) and more complex behaviours such as crack growth and spalling resistance. The design of better coatings requires a predictive understanding of how the microstructure depends on the manufacturing process. A crucial observation for modelling is that the timescale for a particle to splash and cool (about $10\ \mu\text{s}$) is about a tenth of the mean time between the arrivals of particles at a given point. It makes sense to treat the splashing process of each particle in isolation, so the coating is built up through isolated splashing events. Studies of splashing have been made experimentally^{53,54} and theoretically⁵⁵ as a function of droplet speed and temperature.

These, with information from experiment and theory on how the parameters of the plasma torch affect droplet behaviour⁵⁴, enable one to set up rules for splashing and the build-up of a coating⁵⁶. This strategy links the coating microstructure to the process that produced it. But what of its properties? One option is an extended effective medium theory⁵⁷, following the original ideas by Eshelby. This approach provides averaged properties using statistics of the porosity distribution. Many realizations of the microstructure are still needed for reliable statistics of pore distributions and geometries. A second route directly simulates the microstructure's evolution under load using finite element methods, hence obtaining a distribution of possible behaviours, such as propensity to fracture. Overall, we see that appropriate scales are set by droplet size and arrival time. Given these scales, simulations produce microstructures; these microstructures determine properties. The importance of these simulations lies in the direct link offered between the set of parameters describing the plasma gun and the properties of the resulting coating. A data bank of simulations can be built up, such that the process can be inverted. Given the required coating properties,

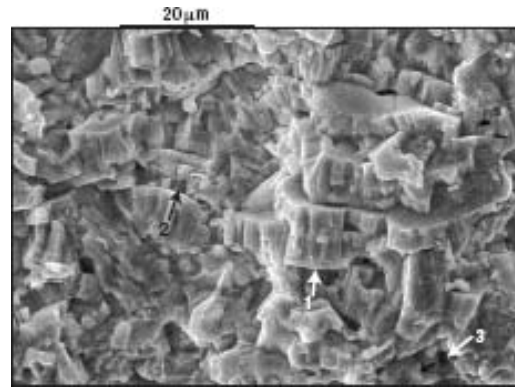


Figure 6 – Microstructure in a plasma-sprayed thermal barrier coating. The structure of the coating is made up of splats a few micrometres thick. The columnar crystal growth (1) shows the direction of heat flow during the rapid cooling of the splats after the ceramic droplets splash onto the surface. Note also the microcracks and voids (2) forming at the splat interface. Some signs of partial melted particles (3) can also be seen. (Scanning electron micrograph courtesy of Paolo Scardi, Dept. of Engineering, University of Toronto.)

what are the parameters of the plasma gun that will produce them? This approach has been demonstrated in principle, using a genetic algorithm to act as a search engine⁵⁶. It is a striking example of what can be achieved with mesoscale modelling. A strategy for predictive modelling of plasma-sprayed coatings is outlined in Fig. 7.

CONCLUSIONS

For many properties and systems, materials behaviour is dominated by mesostructure. The key ideas are not those emphasized in the well-known macroscopic and atomistic approaches. For practical routes to improved performance or processing, one needs a different approach. A small number of the strategies outlined here make it possible to create realizations of microstructures, to understand and predict materials performance, and to select improved processing routes. It does not suffice to create a microstructure that merely looks like that observed. There seems limited call for supercodes solving problems simultaneously at the macro-, meso- and atomic scales. What does seem important is concentrating on the appropriate scale — not too big, not too small.

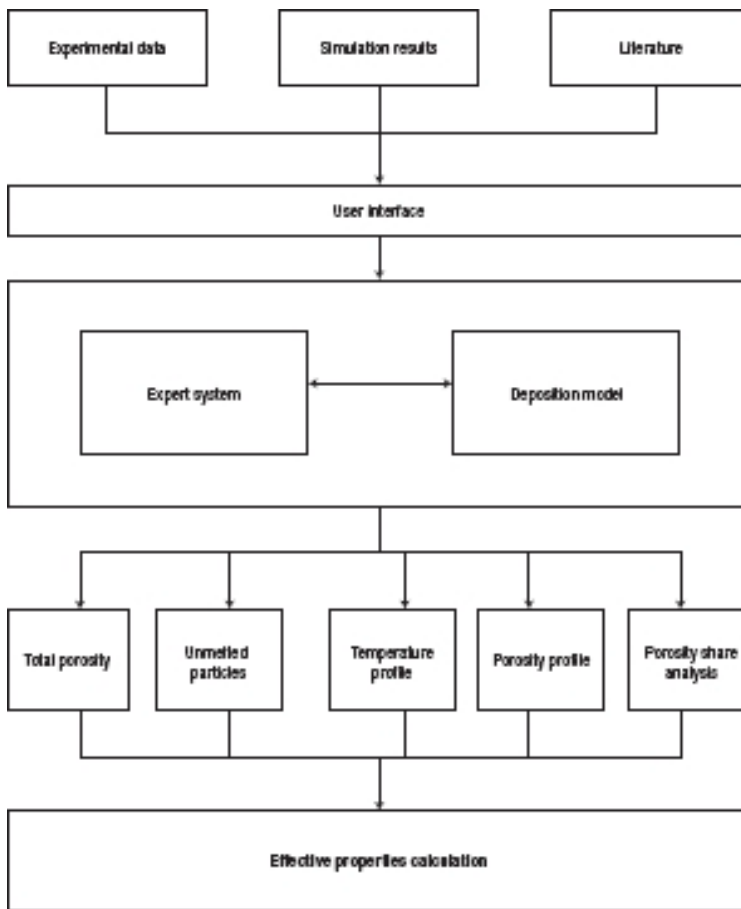


Figure 7 – Strategy for predicting the properties of plasma-sprayed coatings⁵⁶. This shows how the deposition model can be used to drive an expert system that can map out regions of different coating behaviour depending on the different parameters used in producing the coating.

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