

On the paradigm of Hierarchically Structured Materials, in conjunction with the Virtual Special Issue on *Functional Materials*

In recent years, materials engineering community has been developing increasing interest in the topic of hierarchical structuring [1]. Reasons for this direction of onslaught in research are clear: in the quest to deliver the combination of disparate and sometimes mutually contradicting properties of materials, components and structures, researchers seek to ensure the simultaneous presence of the desired structural organisation at all dimensional levels. For example, control over nanoscale arrangement of material building blocks is important for photonic, electrochemical, corrosion and catalytic performance, whilst micron scale architecture determines permeability and acoustic response, and all of these feed into the overall macroscopic properties, such as strength and durability.

We understand hierarchical structure as the conjunction of material architecture at each dimensional level (from molecular through nanometre and micro- to macro-) that underlie the cascade of complex multimodal interactions between material volumes of different nature – electron bands, crystallites ('grains'), grain boundaries, amorphous regions, phase interfaces, defects and impurities, outer surfaces and internal pores, etc. All of these physical entities interact with the external static and dynamic forces and energy flows, and determine the performance of material or devices in terms of specific function(s) and applications.

The search for optimal multi-level structuring is closely related to the biomimetic agenda: Nature provides numerous examples of successful designs that concurrently satisfy multiple requirements of living organisms [2,3]. Consequently, researchers seek to emulate natural designs in their search for new functional and structural materials. Much of this search is application-specific, and is guided by the immediate needs that arise in a particular situation, rather than by some sort of fundamental overarching principles. Without attempting to capture any of these in the present short note, we make here some observations on this matter.

One of the most striking aspects of natural hierarchical structures is the fact that they do not arise as a consequence of equilibrium thermodynamics approach to a global minimum of Gibbs free energy. Non-equilibrium thermodynamics of Onsager and Prigogine demonstrated that systems that exist under the conditions of flow of energy and matter may create highly ordered complex structures with extraordinary properties (and even life itself!). One possible conclusion that may be drawn from this observation is that the creation of multi-level hierarchical structuring *requires* far-from-equilibrium processing. Examples of such can already be found in the modern and classical metallurgy and materials science: martensite laths that confer outstanding hardness and strength on steel components are formed upon rapid cooling from austenitic field. In nickel-base superalloys, the rate of cooling from supersolvus heat treatment temperature determines the size distribution and morphology of the population of secondary and tertiary γ' precipitates.

Whilst these phenomena are well-known and even widely used in engineering practice, experimental characterisation and quantitative description across the range of structural levels remains elusive, primarily due to the challenging nature of the techniques that are well suited for this task. The ability to probe appropriately the fine scale properties of materials and systems requires the combination of utmost spatial and temporal resolution, and relies on the use of such advanced methods as synchrotron and X-ray free electron laser scattering and imaging, electron and ion beam microscopy, etc. Moreover, the need for employing these

costly and complex methods sometimes comes into question, with advanced numerical modelling being offered as an alternative.

In order to counter with viewpoint, we need to bring into our discussion the very definition of what constitutes a structural hierarchical level, and how it can be identified. In the literature, this important question is often addressed in an *ad hoc* fashion, with levels of description defined e.g. by the choice of modelling framework used, such as continuum finite element modelling, dislocation theory, or molecular dynamics (Fig.1).

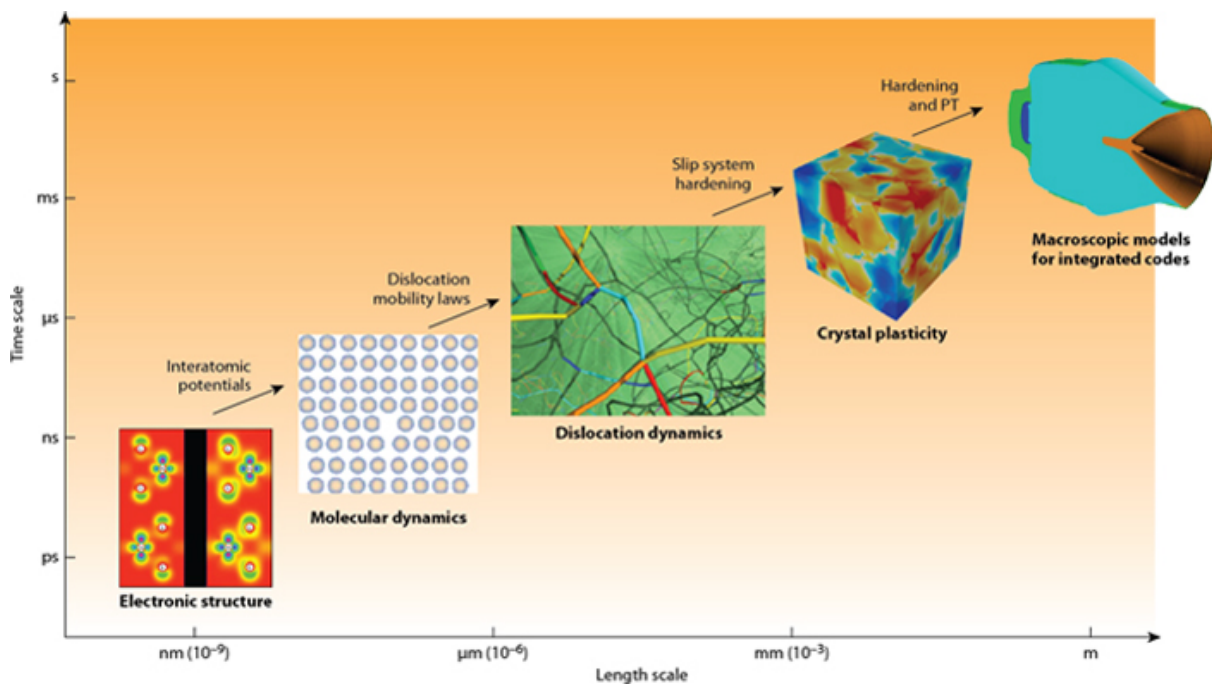


Figure 1. Multi-scale materials modelling (LLNL [4]).

At first sight, this classification approach may appear somewhat superficial: why should the mode of description chosen by the human observer determine the structural organisation hierarchy of a physical material? The key to obtaining insight into this relationship lies in the fact that a numerical or theoretical model may only be accepted and adjudged satisfactory if it displays good agreement with observation, and possesses predictive capabilities. Clearly, the modelling approaches accepted for each structural level possess these characteristics. This means that they capture correctly the underlying physical laws that define the system response at the chosen level.

Additional insight into this complex matter can be obtained by employing the theorem of power law scaling given e.g. by Bažant [5], namely, that as long as the underlying physical laws remain unchanged under the variation of sample size within a given range, the dependence of physical parameters and properties on this size must be described by a power law. Since it is the combination of all such underlying physical laws that defines the modelling framework, it is no surprise that each hierarchical structural level ends up being described by a certain (or several) kinds of simulation frameworks. It is of further interest to enquire what happens when different physical laws come into play with the system upscaling or miniaturisation. For example, when nanoscale description needs to be developed, the proportion of material elements (atoms) lying at surfaces and interfaces increases drastically in comparison with those lying in the bulk of the material. Consequently, whereas at micro- and larger scales such physical terms as surface energies and surface stresses could have been

rightfully neglected, upon “zooming in” to the nanoscale the appropriate description must include these effects.

The transition between different power laws itself also requires careful analysis and description. In fact, it is precisely when such transitions happen that deviation from power law scaling are observed, and referred to as the size effect. This issue has been discussed and addressed with particular application to the case of material strength [6], in which the concept of “knee function” has been introduced, which turns out to be closely related to the functional description proposed by Archibald Hill in a different context [7].

Therefore, the first important conclusion that we draw from this discussion is that levels of hierarchical structuring can be defined by associating them with the range of dimensions for which certain combination of physical laws prevail, reflecting in power law scaling. Transitions between these structural levels correspond to changes in these laws, with the size thresholds being conveniently defined by intercepts between power law scaling trends.

The second conclusion should be made concerning the relationship between modelling and experiment. Since each structural level is described by its own unique combination of physical laws that is distinct from those that prevail at the coarser and finer scales, experimental determination of system parameters must necessarily be conducted at the appropriate spatial resolution to ensure model calibration and validity.

Our comments given above may encourage the readers to take the viewpoint of hierarchical structured materials characterisation and modelling in viewing the Virtual Special Issue (VSI) on Functional Materials introduced below.

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The manuscripts submitted for consideration and publication in the VSI collection on Functional Materials were drawn from the presentations made at the International Conference on Advances in Functional Materials (AFM), held at the University of California, Los Angeles, USA on 14-17 August, 2017. In line with the editorial practice of *Materials & Design*, this collection was further enhanced and extended with contemporaneous submissions to the journal received during the period of preparation of this VSI. As a consequence, the collection of articles produced under the umbrella of this VSI presents a broader and more complete picture of the research landscape in the field.

The thematic coverage of this VSI is broad, and reflects the rich and lively nature of research in the area of functional materials for applications comprising environmental remediation (removal of dyes and pollutants), energy storage and fuel cells, shape memory and phase change materials, piezoelectric sensors and actuators, optical and photonic performance and band gap engineering, electromagnetic, plasmonic and photovoltaic devices, 2D materials, p-n junctions and light-emitting diodes, nanowires, nanotubes, nanoparticles and quantum dots, catalysis, microfluidics and 3D printing, and biocompatibility and medical dosimetry.

The theme of hierarchical structuring runs as a thread through this collected body of research. For example, at molecular dimensional level this theme is reflected in the discussion of optimal conformational structures in the fullerene – polymer pairs in organic photovoltaic cells that theoretically promise power conversion efficiency over 10 % for Pff4TBT/

PBTff4T/, and PNT4T/fullerene pairs [8]. The underlying physical effects define the requirements that the binding energies between monomers, and between fullerene and monomers should be relatively close in value to prevent phase separation that would decrease charge transport across the active heterogeneous layer. This is reached due to the spatial co-ordination of molecular objects having sizes of 1 nm order.

The nanometric dimensional level offers further opportunities for hierarchical structuring and versatile effects contributing in the performance of functional materials. Increasing the space scale the hierarchical structuring of 2D and 3D objects becomes possible. For example, 2-3 nm-thick CVD-grown $100\mu\text{m}\times 100\mu\text{m}$ MoS₂ films followed by single layered graphene layers were vertically stacked on PET substrate to demonstrate the capability of manufacturing of 1cm^2 large photodetectors [9]. A strong dimension correlation with the underlying physics was found, namely, that when potential is applied between the side-gate and the graphene/MoS₂ channel, an electric double layer (EDL) is formed due to the accumulation of free ions at the interface in the (PEO: LiClO₄ =8:1) electrolyte. Considering the large interfacial capacitance of the EDL, the compensation of these charges causes a shift in the Fermi level that is much greater than the value achieved by standard dielectric gates. Hierarchical structure of stacked zones promotes a distinct physical mechanism and enables the enhanced performance of photodetector.

The decoration of a 1-2nm-thick graphene layer with 40-80 nm diameter TiO₂ and Fe₃O₄ nanoparticles creates a hierarchy of objects that is responsible for improved gas sensitivity (down to 5 ppb for benzene) and unexpected correlation between UV irradiation and sensitivity to oxygen [10]. Although the main mechanisms of the underlying phenomena need to be investigated more deeply, these demonstrations reveal significant application potential. Further emphasis on the optimization of nanoparticle structure and size distribution may improve performance by optimising the combination between gas molecule free path and illumination wavelength.

In the fabrication of planar structures, it is natural to consider combining different layers for the creation of new functional materials. Additional layers and induced defects [11, 12], the variation in thickness [13] and chemical composition through copolymerization [14], implantation or sputter doping [15, 16] vary the structure, introducing a number of sub-elements (dots or layers) with dimension in the 1-200 nm range, ultimately allowing fine tuning of the performance.

As a metaphor for hierarchical structuring, the Russian doll (matryoshka) may be rather limited, in that it embodies a nested arrangement of objects of identical shape only. Nevertheless, extending this simple principle offers substantial gains in the performance of functional materials. Multilayered core-shell silica composite nanoparticles (Fe₃O₄@SiO₂@mSiO₂-SiCDs) were prepared by the modified sol-gel method and further immobilized with organosilane-functionalized carbon dots (SiCDs) [17]. The core 50 nm Fe₃O₄ particles were gradually covered with silica shells to reach 500 nm diameter, and outer mesoporous silica shell was stabilized with 2.5-5 nm SiCDs. The resulting Fe₃O₄@SiO₂@mSiO₂-SiCDs nanoparticles had tunable response, i.e. their aqueous solutions exhibited blue light emission with the maximum wavelength of 470 nm at lower concentrations, and red-shifted to yellow-green light emission with the maximum wavelength of 565 nm at higher concentrations. Cell viability tests revealed good biocompatibility of these nanoparticles. Moreover, the concentration of nanoparticles in cytoplasmic matrix or cell organelles could be easily detected at $\lambda_{\text{ex}} = 360$ nm according to the concentration-

dependent fluorescence shifting property, allowing mapping of biological processes. Potentially these nanoparticles can be used for fluorescence sensing in cell counting or in studies of drug delivery and intake. In the biomimetic context, it is interesting to mention that much more sophisticated, hierarchically nanostructured natural silica objects – the famous diatom frustules – employ several specific mechanisms by which they protect the living cell from detrimental UV radiation: absorption by amorphous porous silica; light collection inhibition by diffraction; wavelength conversion and shift by means of photoluminescent emission [18].

Similar multilayered 200-500 nm nanoparticles with Fe oxide cores produced using liquid phase methods were designed to act as sorbents for the removal of dyes [19], biocompatible micro-fluid devices (valves and filters) with potential for blood vessel manipulations [20], photocatalysis [21]. Conversely, nanoparticles with soft / porous core and hard shells of similar dimensions were designed for heat and energy related applications (energy storage and insulation) [22-24]. Even simplest instances of hierarchical structuring such as the creation of multilayered core-shell structures was shown to bring out a whole range of structure-dependent effects potentially applicable in functional materials.

Long tubular quasi-1D objects such as carbon nanotubes as a means of hierarchical structuring offer a broad range of opportunities for tailoring the functional properties through manipulating with the geometry (aspect ratio, curvature, entanglement) and property gradients. A number of interesting cases was demonstrated in the piezoelectric [25], fuel cell [26] and electrochemical energy storage [27] applications.

The creation of 3D objects with specific hierarchy may rely on the combination of methods above, but remains very challenging, involving specific approaches exemplified in [28]. Janus-like fluorescent hybrid particles with sides of different polarity were produced by radical polymerization at the surface of methyl methacrylate (MMA) with Br-modified carbon dots as initiator, and consequent PEGylation via click chemistry. Anticancer drug Doxorubicin (DOX) was found to form 270 nm nanoassemblies with Janus-like hybrids to be deliberately released under pH control with high efficiency.

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The paradigm of *Hierarchically Structured Materials* (HSM) is becoming progressively widely adopted by the scientific community in various domains, ranging from structural to functional applications. This is due to the fact that high performance design must exploit all available elements, structural levels and phenomena through carefully controlled subordination to obtain the desired combination of inherent properties and function in the final design.

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