ON THE MULTISCALE HIERARCHY IN MATERIALS SYSTEMS

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Abstract
Structural heterogeneity and hierarchy are inherent features in biological nature materials, but their significance in dictating the system behaviors is not well understood. This article summarizes several examples to not only explore the underneath geometrical, mechanical, thermal and transport mechanisms, but also stress the ways in which such mechanisms can be applied to developing engineered material systems with novel properties.

Introduction

Our worlds, both natural and social, are structured or arranged in a hierarchal format. For human society, such a hierarchy, being a human creation, has presumably evolved to be beneficial to facilitating communication and management. However, for natural systems such as a tree, a polymer gel, or a vascular system in a biological body, the significance or usefulness of a branched conformation is not always as obvious and has therefore attracted extensive interests. Accumulated research on this has led to several general suppositions, including the self-assembly theories (Whitesides and Grzybowski 2002; Srivastava, Santos et al. 2010), and the fractal theories (West, Brown et al. 1999b; Brown, Gupta et al. 2002). Some even explored certain underlying invariants in these systems in terms of allometric scaling laws (West, Brown et al. 1997; Kuhnert, Helbing et al. 2006) to examine possible shared common features in biological, material and even societal systems at various structural scales.

Self-assembly in the classic sense can be defined as the spontaneous and reversible organization of molecular units into ordered structures by non-covalent interactions (Whitesides, Mathias et al. 1991). The first property of a self-assembled system this definition suggests is the spontaneity of the self-assembly process: the interactions responsible for the formation of the self-assembled system act on a strictly local level—in other words, the nanostructure builds itself. Three factors characterize a self-assembling process and the resultant structure, i.e., order, interactions and building blocks or constituents (Whitesides and Boncheva 2002).

Hierarchy in a material system is represented by several structural characteristics. The first lies in the form of multiscale, i.e., the systems consists of different structural levels with gradual transition in sizes between them. In turn this multiscale always brings in multiple phases (or heterogeneity) into the system where each phase occupies a structure level so as to distinguish one from another. So it is assumed self-evident the term "phase" is used here more generally as representing a structure unit distinctive from its neighbors. We will in this paper examine how such multi-scaling, heterogenizing or multi-phasing are advantageous or useful, to account for the associated unique functionalities in many materials systems.

The importance of structure on material performance is probably best highlighted in the emerging metamaterials which are defined as materials that acquire their unique properties nonexistent in nature, not through chemical modification but through structural alternations (Smith, Pendry et al. 2004; Padilla, Basov et al. 2006; Caloz 2009; Lu, Feng et al. 2009).

Starting from mechanical properties, impact of scale, heterogeneity or hierarchy on material strength has been the essential focus of fracture mechanics, where structural irregularities have been established as the main loci for and contributors to material failure. Lakes (Lakes 1993) studying material hierarchy, used the relative density ρ / ρ_o to reflect the structure efficiency (ρ the system bulk density and ρ_o the density of the material forming the system), for which the Eiffel Tower is 1.2×10^{-3} versus 5.7×10^{-3} for the late World Trade Center. This ratio (or the more commonly used volume fractions) has been widely used in characterizing multi-phased systems and implied the fact that very often, like in the above two cases, air makes up the additional volume in the structure. (*Actually the critical contribution of air residing in a structure is often ignored or grossly underappreciated, as will be demonstrated and elucidated later in the present paper.*) Lakes also discussed the hierarchies existing in polymers, fibrous composites, biological materials and inorganic crystalline materials and pointed out that the distributed interfaces and finer structural features give rise to desirable properties such as stress attenuation and damping, viscoelasticity, superplasticity, increased toughness (fracture resistance) and other benefits. More recently, Fratzl and Weinkamer have reviewed (Fratzl and Weinkamer 2007) the hierarchical biological structures as fiber composites and related their exceptional mechanical properties to a "functional adaptation of the structure at all levels of hierarchy".

The effect of system heterogeneity becomes the central theme in dealing with composite structures (Rosen 1964; Zweben and Rosen 1970; Sutherland, Shenoi et al. 1999; Weiss 2001; Carpinteri, Cornetti et al. 2006; Sun, Gibson et al. 2009) where interactions between the distinct components through interfaces are chiefly responsible for the reinforced synergistic system performance. At nanoscale, structural hierarchy and heterogeneity are reported (Tai, Dao et al. 2007) to be responsible for the improved elasticity, strength and fracture toughness of bones. Nanoscale hierarchy is also found to control the stiffness, strength and mechanical toughness of silk (O'Brien, Fahnestock et al. 1998; Vollrath and Knight 2001; Zhang and Liu 2005; Heim, Romer et al. 2010). In fact the influences of hierarchy permeate into various aspects of material properties and many supposedly intrinsic properties like the thermal and electric conductivities, elastic moduli and dielectric permittivity are actually functions of structural characteristics such as system dimensions, component shape, scale, orientation and interactions (Wang and Pan 2008).

Such explorations of influences due to hierarchy have also taken place in research on other material properties. For instance, surface hierarchy and morphologies are found responsible for super-hydrophobicity (Sun, Luo et al. 2005; Zhao, Lu et al. 2007) and self cleaning – the lotus leaf effect (Cassie and Baxter 1944; Marmur 2004; Burton and Bhushan 2005; Furstner, Barthlott et al. 2005; Gao and McCarthy 2006; Ma and Hill 2006; Koch, Bhushan et al. 2008). Structural photonics employs differential structural scales or hierarchies to generate color without resorting to chemical dyeing (Mason 1926; Denten 1970; Prum, Torres et al. 1998; Srinivasarao 1999; Kinoshita, Yoshioka et al. 2002; Parker, Welch et al. 2003; Vukusic and Sambles 2003; Zi, Yu et al. 2003; Parker 2004; Kinoshita and Yoshioka 2005; Kinoshita, Yoshioka et al. 2008; Yi, Zhu et al. 2008). These are examples of the benefits associated with heterogeneity and hierarchy to either enhance performance or to render new functionalities.

As in materials science, the structure–function relationship remains one of the fundamental issues in biology (Bargel, Koch et al. 2006) where, implicitly or explicitly, structural hierarchies have been extensively investigated and are believed to account for various unique attributes observed. For example, geckos use fibrous adhesive on their feet to acquire superior surface attachment without losing their movement agility (O'Brien, Fahnestock et al. 1998; Autumn, Liang et al. 2000; Geim, Dubonos et al. 2003; Hansen and Autumn 2005; Lewis 2006; Tian, Pesika et al. 2006; Autumn and Gravish 2008; Zeng, Pesika et al. 2009; Zhao, Pesika et al. 2009) It was reported that the unique macroscopic orientation and preloading of gecko foot-hair increased the attachment force 600-fold above that of normal friction of the material(Autumn, Liang et al. 2000).

In general, learning from nature or bio-inspired technology has always been a very effective approach for human creativity. In naturally formed biological systems, "One of the major problems confronting modern biology is to understand how complex morphological structures arise during development and how they are altered during evolution" (Atchley and Hall 1991). Owing to the ever-increasing demand of changing environment and competition for survival, biological systems have evolved to optimize their functionality, and the resulting hierarchies in plants, animals, physiological systems are logically manifestation of high efficiency and adaptability. It is therefore up to us to explore, decode and understand the accumulated efficiency embedded in such systems, and to apply the new knowledge for society's benefit. One added advantage in bionics is that "… the design rules from Nature can be extended into non-biological environments once moved into a laboratory setting and less constrained by the requirements for survival of living organisms (Li and Kaplan 2003)."

Based on existing work on underlying laws in various structural systems, West et al (West, Brown et al. 1997; West, Brown et al. 1999a) proposed a few allometric scaling relations, including the 3/4 power law for metabolic rates derived from a general model. They believe that these laws are characteristic of all organisms and show how the essential materials are transported through space-filling fractal networks of branching tubes, as shown in Figure 1(West, Brown et al. 1997; West, Brown et al. 1999a). They also expanded their scaling laws to forests (West, Enquist et al. 2009) and even human societies(Bettencourt, Lobo et al. 2008).

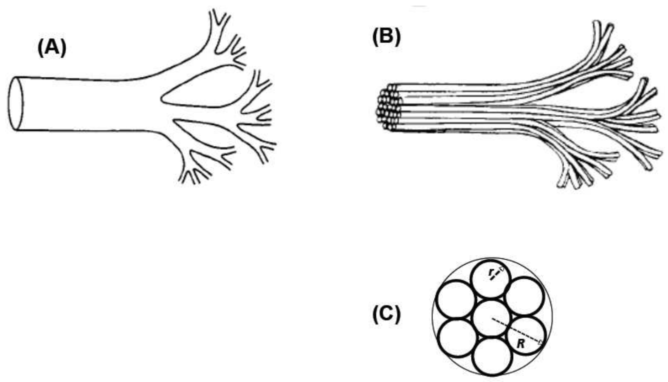

Fig. 1. Diagrammatic examples of segments of biological distribution networks: (A) mammalian circulatory and respiratory systems composed of branching tubes; (B) plant vessel-bundle vascular system composed of diverging vessel elements; (C) cross section of (B).

However many of the useful applications of hierarchy do not have to be accomplished or manifested at scales invisible to the naked eye or to employ sophisticated instrumentation. This article is an attempt to explore the advantages or added functionalities attributable to system hierarchy, based on simple diagrams like Figure 1, through plain physics and mathematics, and at macro scale.

1. Branching out to increase the specific surface area

A system has to interact with its surroundings. Most if not all such interactions are conducted through its surface. Therefore maximizing surface area for a given mass or volume should likely be one of the advantages in forming a hierarchical conformation. Assuming identical material volume, let's compare the surface areas of two structures - a solid rod of radius *R* and a bundle of total radius *R* but with *N* circular branches each of radius *r*, as in Figure 1(C). It is readily demonstrated that $R = \sqrt{N}r$. Note the specific surface area is the total surface area over its volume. It is easy to show that, when N is large enough, the ratio of the specific areas between the two cases is

$$\frac{A_b}{A_r} = \frac{\sum_N A_i}{A_r} = \sqrt{N} \quad (1)$$

That is the specific surface area for the bundle A_b increases as *N* grows (*r* reduces) and approaches infinity as $N \to \infty$ or $r \to 0$, i.e., structure hierarchy directly increases the system specific area.

2. Structural flexibility

Also from Figure 1, the ratio of the bending moment of inertia between the bundle and rod is

$$\frac{I_b}{I_r} = \frac{\sum_N I_i}{I_r} \to \frac{N\xi\frac{\pi r^4}{4}}{N^2\frac{\pi r^4}{4}} = \frac{\xi}{N} \quad (2)$$

The coefficient ξ, clearly $\leq N$, is introduced here to reflect the constraint between the branches in the bundle, hindering the individual branch from bending over its own axis freely. However, as long as such constraint remains constant or at least not growing at the same order as the number of braches *N*, increasing *N* will considerably reduce the bending stiffness, i.e., the more members in the bundle, the more flexible the system, at given constraint ξ. We all know that by branching out, as opposed to being a single trunk, a tree becomes more resilient against wind. Such heterogenization by bringing air into the system as a buffer increases the system resilience or its fracture resistance.

This reduction in material stiffness due to structural hierarchy also works for shear load. Consider two pieces of materials shown in Figure 2, where (A) is a homogeneous and isotropic membrane, and (B) a piece of woven fabric with finer components.

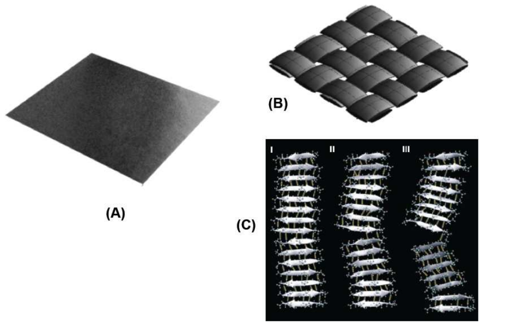

Fig. 2. Hierarchy brings in system flexibility and controlled stiffness: (A) an isotropic plastic sheet; (B) a woven fabric; (C) β-nano crystals sheets in silk.

According to continuum theory, for the uniform membrane (A), the ratio between its tensile modulus E and shear modulus G is related to its Poisson's ratio *v* as:

$$\frac{E}{G} = 2(1+\nu) \tag{3}$$

For normal uniform materials like (A), $0 < \nu < 0.5$ so that $2 < (E/G) < 3$. In other words, for ordinary materials, the tensile and shear moduli are of the same order of magnitude, i.e., shearing the material is not much easier than stretching it. Fortunately, this is not the case for the fabric in (B), it is reported (Bassett, Postle et al. 1999) that its ratio of $E/G \rightarrow 200$, depending on the type of weave structure. In fact, a fabric will shear easily even under its own weight: once a fabric is laid onto an object, it will deform in complex strain state including bending and shear until it covers the object to the degree allowable by this E/G ratio – making woven fabrics irreplaceable as *the* material for comfortable and elegant apparels.

The main reason for such excellent formability of a fabric is due, of course, to the easy relative movement of individual components (yarns) in the fabric, reflected by the unusually small shear modulus *G* value. Twists or entanglements or other frictional form of constraints are the mechanisms in controlling the relative movement between the individual structural members and thus the overall compliance to deformation. In general, ability to accommodating complex stress fields is the main factor in dealing with buckling or wrinkling of membranes (Pocivavsek, Dellsy et al. 2008), including facial skin (McCormick 2007). It is a pleasant surprising therefore to see in a recent paper on studying the mechanical properties of silk. It reports that silk is formed at finer scale with the so-called β-nano crystals sheets shown in Figure 2(C) which is found responsible for among other attributes excellent strength and fracture toughness of the silk fibers, due mainly to the ability of such a flexible nano structure in accommodating various local stresses (Keten, Xu et al. 2010).

Essentially such hierarchy with its attendant interfaces allows the origins of stiffness and toughness in a material to be separated, and thus offers the possibility of independent control. This is impossible in most conventional materials, which have to sacrifice stiffness for toughness, or vice versa. For instance, in a textile woven structure in Figure 2(B), its tensile moduli in the two orthogonal directions E_{xx} and E_{yy} can be adjusted independently as long as:

$$\frac{\nu_{xy}}{E_{xx}} = \frac{\nu_{yx}}{E_{yy}} \tag{4}$$

where v_{xy} and v_{yx} are the associated Poisson's ratios (Agarwal and Broutman 1990), an advantage exhibited by many membranes in biological systems (like in bird's wings and duck's feet) but difficulty to achieve in regular engineering materials.

Furthermore it is common knowledge that, according to the weakest link theory in materials strength, a longer or larger specimen appears weaker. But for given specimens, such size effect is found to be suppressed by an increased local hierarchy, i.e., the ones with finer structural details exhibit more consistent strength values, and are less sensitive to their macro-size (Pan, Zhao et al. 2000).

3. Enhancing liquid transport

It is easy to demonstrate that hierarchy improves wetability of a material (Brochard 1986; Lukas and Pan 2003). We can use the Harkinson spreading parameter (Brochard 1986) for this purpose, which is in general defined as:

$$S = \gamma_s + \gamma_{sl} - \gamma_l \qquad (4)$$

where $\gamma_s, \gamma_{sl}, \gamma_l$ are the surface tensions between solid-air, solid-liquid and liquid-air, respectively. A material will be wetted if its critical Harkinson spreading parameter $S_c \leq S$. This critical parameter for the fiber bundle in Figure 1(C) can be expressed as (Lukas and Pan 2003):

$$S_c = \frac{R - Nr}{Nr}\gamma_l = \frac{\sqrt{N}r - Nr}{Nr}\gamma_l = (\frac{1}{\sqrt{N}} - 1)\gamma_l, \qquad (5)$$

and decreases as *N* increases. That is, for a given mass of material, making it into a fiber bundle containing finer fibers will significantly enhance its wetability.

4. Behavior non-affinities between different structural levels

Once branching out occurs, other interesting phenomena take place as well. One can be called the non-affinity, i.e., seemingly disconnection between the macro-properties and the corresponding properties of its constituents. Just as nanoparticles display properties that differ from those of the bulk samples of the same material, ensembles of nanoparticles can have collective performance that deviates from that displayed by *both* the individual nanoparticles and the bulk samples (Du, Heldebrant et al. 2002; Nie, Petukhova et al. 2010). Such non-affinity is in fact the inherent consequence, and often induced advantages, from the structural hierarchy.

For instance in thermal performance, the same cotton fibers can be made into a thin and cool T-shirt for summer or a thick and warm flannel coat for winter. That is, the thermal attribute of the final product seems to be independent of the thermal properties of its components (the fibers). Further analysis however reveals that our sensed warmth is actually determined by a composite parameter termed the thermal effusivity (Mandelis 1991), defined as:

$$\varepsilon = \sqrt{k\rho c_p} \qquad (6)$$

The definitions and the possible ranges of the parameters are provided in Table 1 (Pan 2007).

Table 1 Possible ranges of the parameters

Property	unit	minimum	maximum	Range ratio
Thermal conductivity	k (W/m-K)	> 0.03	0.1	< 4
Density	ρ (kg/m^3)	> 1.23	200	< 160
Specific heat capacity	c_p (J/kg-K)	>0.3	<1.0	< 4

During the manufacturing process in converting fibers into final products, both thermal conductivity k and specific heat capacity c_p change very little and their ranges given in the table actually are the estimated maximum possibilities. The only parameter in Equation (6) capable of accounting for the huge diversity in the thermal performance of the products is the bulk material density ρ which can alter as shown in the table by a few hundred times – the kind of density difference observed in between our T-shirts and flannel coats. The secret of the heat retention lies of course in the still air contained in the much more porous flannel coat, for still air is the best thermal insulator. Enclosing air and keeping it still is the most effective way to generate super thermal protection, a very plausible explanation for the hollow fibers seen in Figure 3 forming the fur for polar bears.

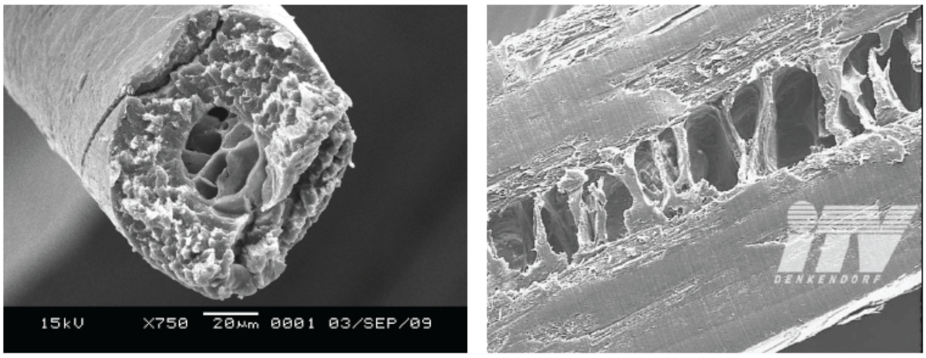

Figure 3 The hollow fiber in polar bear fur.

Here is another example how air plays a dominant role in determining material performance. For the cushion under compression in Figure 4(A), the compression stiffness E_c is known (Carnaby and Pan 1989) to scale to the cubic of the fiber volume fraction V_f as:

$$E_c : E_f V_f^3 \quad (7)$$

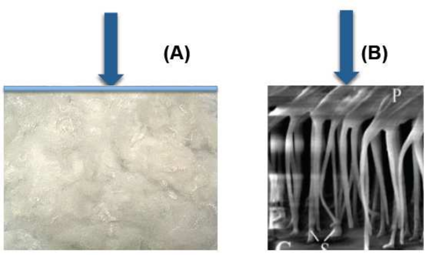

Fig. 4. Hierarchy brings in system softness: (A) a fibrous cushion; (B) a portion of the foot of a fruit fly.

where E_f is the axial modulus of the solid fiber itself. Equation 7 indicates that by building a fibrous cushion to incorporate large amount of air - the unconfined air here presents very low compression resistance - as reflected by $V_f = 1$, the macro compression resistance is markedly reduced comparing to the fiber modulus E_f, as shown in Equation 7. A closer observation reveals that because of the existence of air in the pores between fibers, when the cushion is under macro-compression, individual fibers are in fact experiencing bending deformation – another example of the behavior non-affinity. Furthermore, because of its thin cross section, the bending resistance of the fibers is very low, leading to the soft cushioning effect, something seemly manifested in fruit flies feet illustrated in the photo (Gorb 1998) of Figure 4(B), for the same cushioning effect.

Although the mechanical resistance of air when confined in a tire or a basketball, or the associated importance of confined air in many applications is hard to deny, air or moisture is still more often viewed as "empty" or "nothing", and thus leads to erroneous predictions in analyzing related systems. To further elucidate the significance of this issue, here are a few notes. First because of the omnipresence of air and moisture, they often constitute individual phases in a multiphase system. Although frequently un-intentioned, they nonetheless play deciding roles in determining the behaviors of the system under various external stimuli, owing to the huge extremity in their properties as exemplified in Table 2. On the other hand, heterogenization in material design to purposely include air and/or moisture can be highly efficient to achieve otherwise unachievable functions - the superior thermal and electric insulation of air has already found extensive applications. Note in particular from Table 2 the time dependent nature of the shear moduli for both air and water, which can further increase the potential and sophistication in such material performance manipulation, if used properly.

Table 2 Properties comparison

property	polymers	water	air
Density (g/cm^3)	0.8	1	0.001
Bulk modulus (GPa)	5	2.2	1x10^{-4}
Thermal conductivity (W/m·K)	0.07	0.6	0.025
Electrical Conductivity (S·m^{-1})	< 10^{-6}	5*10^{-4} ~5*10^{-2}	~ 0
Shear modulus (GPa)	0.8	$\frac{\eta_w}{t}$	$\frac{\eta_a}{t}$

η **is the viscosity of the fluid.**

(The data in the table are estimations for discussion only and more specific ranges can be verified online easily.)

Finally it may be handy to end this paper by citing from a recent review article on hierarchical construction of self-assembled low-dimensional molecular architectures (Yang and Wang 2009). "Hierarchical molecular assembly has drawn increasing interest in recent years because of the possibility of fabricating highly ordered functional superstructures from elemental building units … without synthesizing the whole structure bond-by-bond. It is still challenging to fully understand the principles governing the transition from elemental building units to higher level assemblies and even macroscopic systems." Yet, such connections between structure and functionality are clearly easier to show and appreciate at macro-scales, as, hopefully, demonstrated through the present report.

Conclusions

Hierarchy, multiphase and multiscale in natural materials are not accident but a manifestation of adaptation and optimization through the evolution process. It should be better studied, understood and more importantly utilized in our engineering designs for more efficient materials with novel properties. We have first demonstrated in this article that structure hierarchies directly increase the system specific area, improve the mechanical flexibility and enhance the system hydrophilicity. Also, it becomes much easier, in a hierarchical system, to adjust properties independently so as to tailor to our needs. Furthermore, we stressed an interesting phenomenon in multiphase hierarchical material structures, i.e., seemingly disconnection between the macro-properties and the corresponding properties of its constituents. Then because of the often huge distinctions in properties of the constituents in different phases in a composite system, one can manipulate the distribution and relative proportion of each phase to optimize the system behavior. Because of the omnipresence of air and moisture in materials, their contributions should not be underestimated.

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References Cited:

- Agarwal, B. D. and L. J. Broutman (1990). Analysis and Performance of Fiber Composites. New York, Wiley-Interscience.
- Atchley, W. R. and B. K. Hall (1991). "A model for development and evolution of complex morphological structures." Biological Reviews of the Cambridge Philosophical Society **66**(2): 101-157.
- Autumn, K. and N. Gravish (2008). "Gecko adhesion: evolutionary nanotechnology." Philosophical Transactions of the Royal Society a-Mathematical Physical and Engineering Sciences **366**(1870): 1575-1590.
- Autumn, K., Y. A. Liang, et al. (2000). "Adhesive force of a single gecko foot-hair." Nature **405**(6787): 681-685.
- Bargel, H., K. Koch, et al. (2006). "Structure-function relationships of the plant cuticle and cuticular waxes - a smart material?" Functional Plant Biology **33**(10): 893-910.
- Bassett, R. J., R. Postle, et al. (1999). "Experimental methods for measuring fabric mechanical properties: A review and analysis." Textile Research Journal **69**(11): 866-875.
- Bettencourt, L. M. A., J. Lobo, et al. (2008). "Why are large cities faster? Universal scaling and self-similarity in urban organization and dynamics." European Physical Journal B **63**(3): 285-293.
- Brochard, F. (1986). "Spreading of liquid-drops on thin cylinders - the manchon-droplet transition." Journal of Chemical Physics **84**(8): 4664-4672.

- Brown, J. H., V. K. Gupta, et al. (2002). "The fractal nature of nature: power laws, ecological complexity and biodiversity." Philosophical Transactions of the Royal Society B-Biological Sciences **357**(1421): 619-626.
- Burton, Z. and B. Bhushan (2005). "Hydrophobicity, adhesion, and friction properties of nanopatterned polymers and scale dependence for micro- and nanoelectromechanical systems." Nano Letters **5**(8): 1607-1613.
- Caloz, C. (2009). "Perspectives on EM metamaterials." Materials Today **12**(3): 12-20.
- Carnaby, G. A. and N. Pan (1989). "Theory of the compression hysteresis of fibrous assemblies." Textile Research Journal **59**(5): 275-284.
- Carpinteri, A., P. Cornetti, et al. (2006). "Scaling laws and multiscale approach in the mechanics of heterogeneous and disordered materials." Applied Mechanics Reviews **59**(1-6): 283-305.
- Cassie, A. B. D. and S. Baxter (1944). "Wettability of porous surfaces." Transactions of the Faraday Society **40**: 0546-0550.
- Denten, E. J. (1970). "REVIEW LECTURE - On organization of reflecting surfaces in some marine animals." Philosophical Transactions of the Royal Society of London Series B-Biological Sciences **258**(824): 285-&.
- Du, C. S., D. Heldebrant, et al. (2002). "Preparation of carbon nanotubes composite sheet using electrophoretic deposition process." Journal of Materials Science Letters **21**(7): 565-568.
- Fratzl, P. and R. Weinkamer (2007). "Nature’s hierarchical materials." Progress in Materials Science **52**: 1263–1334.
- Furstner, R., W. Barthlott, et al. (2005). "Wetting and self-cleaning properties of artificial superhydrophobic surfaces." Langmuir **21**(3): 956-961.
- Gao, L. C. and T. J. McCarthy (2006). ""Artificial lotus leaf" prepared using a 1945 patent and a commercial textile." Langmuir **22**(14): 5998-6000.
- Geim, A. K., S. V. Dubonos, et al. (2003). "Microfabricated adhesive mimicking gecko foot-hair." Nature Materials **2**(7): 461-463.
- Gorb, S. N. (1998). "The design of the fly adhesive pad: Distal tenent setae are adapted to the delivery of an adhesive secretion." Proceedings of the Royal Society of London Series B-Biological Sciences **265**(1398): 747-752.
- Hansen, W. R. and K. Autumn (2005). "Evidence for self-cleaning in gecko setae." Proceedings of the National Academy of Sciences of the United States of America **102**(2): 385-389.
- Heim, M., L. Romer, et al. (2010). "Hierarchical structures made of proteins. The complex architecture of spider webs and their constituent silk proteins." Chemical Society Reviews **39**(1): 156-164.
- Keten, S., Z. P. Xu, et al. (2010). "Nanoconfinement controls stiffness, strength and mechanical toughness of beta-sheet crystals in silk." Nature Materials **9**(4): 359-367.
- Kinoshita, S. and S. Yoshioka (2005). "Structural colors in nature: The role of regularity and irregularity in the structure." Chemphyschem **6**(8): 1442-1459.
- Kinoshita, S., S. Yoshioka, et al. (2002). "Mechanisms of structural colour in the Morpho butterfly: cooperation of regularity and irregularity in an iridescent scale." Proceedings of the Royal Society of London Series B-Biological Sciences **269**(1499): 1417-1421.
- Kinoshita, S., S. Yoshioka, et al. (2008). "Physics of structural colors." Reports on Progress in Physics **71**(7).
- Koch, K., B. Bhushan, et al. (2008). "Diversity of structure, morphology and wetting of plant surfaces." Soft Matter **4**(10): 1943-1963.
- Kuhnert, C., D. Helbing, et al. (2006). "Scaling laws in urban supply networks." Physica a-Statistical Mechanics and Its Applications **363**(1): 96-103.
- Lakes, R. (1993). "Materials with structural hierarchy." Nature **361**(6412): 511-515.

- Lewis, R. V. (2006). "Spider silk: Ancient ideas for new biomaterials." Chemical Reviews **106**(9): 3762-3774.
- Li, C. M. and D. L. Kaplan (2003). "Biomimetic composites via molecular scale self-assembly and biomineralization." Current Opinion in Solid State & Materials Science **7**(4-5): 265-271.
- Lu, M. H., L. Feng, et al. (2009). "Phononic crystals and acoustic metamaterials." Materials Today **12**(12): 34-42.
- Lukas, D. and N. Pan (2003). "Wetting of a fiber bundle in fibrous structures." Polymer Composites **24**(3): 314-322.
- Ma, M. L. and R. M. Hill (2006). "Superhydrophobic surfaces." Current Opinion in Colloid & Interface Science **11**(4): 193-202.
- Mandelis, A. (1991). "Photothermal applications to the thermal-analysis of solids." Journal of Thermal Analysis **37**(5): 1065-1101.
- Marmur, A. (2004). "The lotus effect: Superhydrophobicity and metastability." Langmuir **20**(9): 3517-3519.
- Mason, C. W. (1926). "Structural colors in insects. I." Journal of Physical Chemistry **30**(3): 383-395.
- McCormick, S. (2007). "Materials science - Exploiting wrinkle formation." Science **317**(5838): 605-606.
- Nie, Z. H., A. Petukhova, et al. (2010). "Properties and emerging applications of self-assembled structures made from inorganic nanoparticles." Nature Nanotechnology **5**(1): 15-25.
- O'Brien, J. P., S. R. Fahnestock, et al. (1998). "Nylons from nature: Synthetic analogs to spider silk." Advanced Materials **10**(15): 1185.
- Padilla, W. J., D. N. Basov, et al. (2006). "Negative refractive index metamaterials." Materials Today **9**(7-8): 28-35.
- Pan, N. (2007). "Quantification and evaluation of human tactile sense towards fabrics." Int. Journal of Nature & Design **1**: 48-60.
- Pan, N., S. M. Zhao, et al. (2000). "Relationship between scale effect and structure levels in fibrous structures." Polymer Composites **21**(2): 187-195.
- Parker, A. R. (2004). "A vision for natural photonics." Philosophical Transactions of the Royal Society of London Series a-Mathematical Physical and Engineering Sciences **362**(1825): 2709-2720.
- Parker, A. R., V. L. Welch, et al. (2003). "Structural colour - Opal analogue discovered in a weevil." Nature **426**(6968): 786-787.
- Pocivavsek, L., R. Dellsy, et al. (2008). "Stress and fold localization in thin elastic membranes." Science **320**(5878): 912-916.
- Prum, R. O., R. H. Torres, et al. (1998). "Coherent light scattering by blue feather barbs." Nature **396**(6706): 28-29.
- Rosen, B. W. (1964). "Tensile failure of fibrous composites." AIAA Journal **2**(11): 1985-1991.
- Smith, D. R., J. B. Pendry, et al. (2004). "Metamaterials and negative refractive index." Science **305**(5685): 788-792.
- Srinivasarao, M. (1999). "Nano-optics in the biological world: Beetles, butterflies, birds, and moths." Chemical Reviews **99**(7): 1935-1961.
- Srivastava, S., A. Santos, et al. (2010). "Light-Controlled Self-Assembly of Semiconductor Nanoparticles into Twisted Ribbons." Science **327**(5971): 1355-1359.
- Sun, L. Y., R. F. Gibson, et al. (2009). "Energy absorption capability of nanocomposites: A review." Composites Science and Technology **69**(14): 2392-2409.
- Sun, M. H., C. X. Luo, et al. (2005). "Artificial lotus leaf by nanocasting." Langmuir **21**(19): 8978-8981.
- Sutherland, L. S., R. A. Shenoi, et al. (1999). "Size and scale effects in composites: I. Literature review." Composites Science and Technology **59**(2): 209-220.

- Tai, K., M. Dao, et al. (2007). "Nanoscale heterogeneity promotes energy dissipation in bone." Nature Materials **6**(6): 454-462.
- Tian, Y., N. Pesika, et al. (2006). "Adhesion and friction in gecko toe attachment and detachment." Proceedings of the National Academy of Sciences of the United States of America **103**(51): 19320-19325.
- Vollrath, F. and D. P. Knight (2001). "Liquid crystalline spinning of spider silk." Nature **410**(6828): 541-548.
- Vukusic, P. and J. R. Sambles (2003). "Photonic structures in biology." Nature **424**(6950): 852-855.
- Wang, M. and N. Pan (2008). "Predictions of effective physical properties of complex multiphase materials." Materials Science & Engineering R-Reports **63**(1): 1-30.
- Weiss, J. (2001). "Fracture and fragmentation of ice: a fractal analysis of scale invariance." Engineering Fracture Mechanics **68**(17-18): 1975-2012.
- West, G. B., J. H. Brown, et al. (1997). "A general model for the origin of allometric scaling laws in biology." Science **276**(5309): 122-126.
- West, G. B., J. H. Brown, et al. (1999a). "A general model for the structure and allometry of plant vascular systems." Nature **400**(6745): 664-667.
- West, G. B., J. H. Brown, et al. (1999b). "The fourth dimension of life: Fractal geometry and allometric scaling of organisms." Science **284**(5420): 1677-1679.
- West, G. B., B. J. Enquist, et al. (2009). "A general quantitative theory of forest structure and dynamics." Proceedings of the National Academy of Sciences of the United States of America **106**(17): 7040-7045.
- Whitesides, G. M. and M. Boncheva (2002). "Beyond molecules: Self-assembly of mesoscopic and macroscopic components." Proceedings of the National Academy of Sciences of the United States of America **99**(8): 4769-4774.
- Whitesides, G. M. and B. Grzybowski (2002). "Self-assembly at all scales." Science **295**(5564): 2418-2421.
- Whitesides, G. M., J. P. Mathias, et al. (1991). "Molecular self-assembly and nanochemistry - A chemical strategy for the synthesis of nanostructures." Science **254**(5036): 1312-1319.
- Yang, Y. L. and C. Wang (2009). "Hierarchical construction of self-assembled low-dimensional molecular architectures observed by using scanning tunneling microscopy." Chemical Society Reviews **38**(9): 2576-2589.
- Yi, Y. P., L. Y. Zhu, et al. (2008). "Theoretical designs of molecular photonics materials." Macromolecular Theory and Simulations **17**(1): 12-22.
- Zeng, H. B., N. Pesika, et al. (2009). "Frictional Adhesion of Patterned Surfaces and Implications for Gecko and Biomimetic Systems." Langmuir **25**(13): 7486-7495.
- Zhang, H. M. and J. Y. Liu (2005). "Molecular architecture and engineering of spider dragline silk protein." Progress in Natural Science **15**(9): 769-776.
- Zhao, B. X., N. Pesika, et al. (2009). "Role of Tilted Adhesion Fibrils (Setae) in the Adhesion and Locomotion of Gecko-like Systems." Journal of Physical Chemistry B **113**(12): 3615-3621.
- Zhao, N., X. Y. Lu, et al. (2007). "Progress in superhydrophobic surfaces." Progress in Chemistry **19**(6): 860-871.
- Zi, J., X. D. Yu, et al. (2003). "Coloration strategies in peacock feathers." Proceedings of the National Academy of Sciences of the United States of America **100**(22): 12576-12578.
- Zweben, C. and B. W. Rosen (1970). "A statistical theory of material strength with application to composite materials." Journal of the Mechanics and Physics of Solids 18(3): 189-&.