Multiscale effects and capillary interactions in functional biomimetic surfaces for energy conversion and green engineering

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Biological surfaces (plant leaves, lizard and insect attachment pads, fish scales, etc.) have remarkable properties due to their hierarchical structure. This structure is a consequence of the hierarchical organization of biological tissues. The hierarchical organization of the surfaces allows plants and creatures to adapt to energy dissipation and transition mechanisms with various characteristic scale lengths. At the same time, an addition of a micro-/nanoscale hierarchical level, for example of surface roughness, can change qualitatively the properties of a system and introduce multiple equilibriums, instability and dissipation. Thus, small roughness has a large effect. In particular, a small change of surface roughness can lead to a large change in the capillary force. The capillary effects are crucial for small-scale applications. Multiscale organization of the biomimetic surfaces and their adaptation to capillary effects make them suitable for applications using new principles of energy transition (e.g. capillary engines) and environment-friendly technologies (e.g. self-cleaning oleophobic surfaces).

Keywords: biomimetics; biomaterials; self-cleaning

1. Introduction

Biomimetics is the application of methods and concepts found in living nature to the study and design of engineering systems (Koch et al. 2008, 2009). The word ‘biomimetics’ was coined in the 1960s by biophysicist Otto Schmitt, while other terms used sometimes are ‘bionics’ (used by J. E. Steele in 1960) and ‘biomimicry’ (Bar-Cohen 2006). Biomimetics goes further than biophysics and bioengineering, since its objective is not just to study biological systems but also to mimic biological objects with desirable properties. The idea behind biomimetics is that nature’s technical solutions are perfect, or at least better than those which contemporary engineering technology can suggest. This concept has been applied to various areas of engineering, ranging from artificial intelligence and neural networks to robotics to biomimetic materials.

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It is important to distinguish between ‘true biomimetics’ (mimicking mechanisms and methods of living nature for engineering purposes) and a simple similarity between biological and technical objects. For example, an aeroplane is similar to a bird as it has wings and a tail. Furthermore, the first plane built by the Wright brothers, as well as earlier less successful models going back to the concept of a flying machine suggested by da Vinci in the fifteenth century, was inspired by birds. However, the principles of plane flight are very different from bird flight, so we do not deal here with borrowing mechanisms or methods found in living nature. In a similar manner, a tank’s armour may have a similar function to a turtle shell; however, the similarity in functionality does not constitute borrowing. Therefore, one should be careful to avoid using the term biomimetics too broadly.

In the biomimetic design of materials, a number of ideas have been suggested covering such diverse areas as biological self-assembly, receptors, protein machines, muscle filaments, microstructured surfaces, artificial cartilage for shock absorption, mucus for solid–fluid transformation, collagen and the use of insect cuticle microstructure for advanced composite biomimetic surfaces to control cell adhesion and drug delivery (Byrne et al. 2002). Unlike humans, biological organisms do not have access to the high temperatures or pressures that are required to produce most technical materials, such as steel, metals, silicon and plastics. Nevertheless, nature has developed many materials with remarkable functional properties that are often superior to engineering materials. The key for these remarkable properties is the complex hierarchical structure of the natural materials (Nosonovsky & Bhushan 2007a, 2008a; Bhushan et al. 2008).

There are several important differences between the ways in which nature and an engineer use materials (table 1). An engineer has a much greater range of available elements, including iron and other metals, while nature has to deal mostly with polymers and composites of polymers and ceramic structures, built of light elements. Nature builds organisms by means of growth or biologically controlled self-assembly, adapting to the environmental condition, and not by the secure design and selection of materials with required final properties, as engineers do. Biological materials are grown without the final ‘design specification’, but by using the recipes contained in the genetic code. As a result, biological materials and tissues are created by hierarchical structuring at all levels, optimizing and adapting form and structure to the function (Fratzl 2007). The genetic algorithm interacts with the environmental condition that provides flexibility. For example, a tree branch can grow differently in the direction of the wind and in the opposite direction. The only way to provide this

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Table 1. The use of materials by engineer and by nature.

| Engineering Materials | Biological Tissues |
|-----------------------|-------------------|
| Wide range of elements including metals | Light elements |
| Manufacturing | Growth and self-assembly |
| Design up to final specifications | Adaptation to environment |
| Usually single-scale structure | Hierarchical structure |
| No ability for self-repair | Self-repair |

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adaptive self-assembly is a hierarchical self-organization of the material. Thus, the difference of natural versus engineering design is the difference of growth versus fabrication.

A remarkable property of biological tissues is their ability for self-healing, which is also related to the hierarchical organization. There are several biological mechanisms of self-repair. At the molecular level, there are dynamically breaking and repairing ‘sacrificial’ bonds, which allow for material to deform in a quasi-plastic manner without fracture. In bones, there is a cyclic replacement of material by specialized cells, which allows for a bone to adapt to changing conditions and to repair damage. Many fractured or critically damaged living tissues can heal themselves by the formation of an intermediate tissue (based on the response to inflammation) followed by the scar tissue (Fratzl 2007).

In the field of biomimetic surfaces, a number of ideas have been suggested so far (Barthlott & Neinhuis 1997; Bar-Cohen 2006; Gorb 2006). These include: the lotus leaf surface that has superhydrophobic and self-cleaning properties; gecko foot that has very high and adaptive adhesion; moth eye that does not reflect light; shark skin that suppresses turbulence while the shark is swimming underwater; pond skater leg that can stay dry; darkling beetle that can collect dew using hydrophilic microspots; and sand skink that can reduce friction using nanothresholds. The common feature found among many of these surfaces is that they have hierarchical roughness with rough details ranging from nanometres to millimetres. Biomimetic solutions for self-healing surfaces have been proposed; for example, a superhydrophobic surface with a reservoir containing a hydrophobic polymer that mimics wax of the lotus leaf and thus combines superhydrophobic and self-healing properties (Blossey 2003).

The central concept of surface science is surface energy. During contact of solid surfaces (e.g. friction) or with liquid (wetting), irreversible energy dissipation occurs, involving many mechanisms that act simultaneously in the bulk of the body (three dimensional), at the solid–liquid or solid–solid contact interface (two dimensional) and at the solid–liquid–air triple line (one dimensional). These mechanisms of dissipation, friction and wetting involve viscosity, adhesion, disjoining pressure and van der Waals force, precursor formation, chemical bonding, elastic and plastic deformation, etc. (Nosonovsky 2007b). These mechanisms have various characteristic length scales and thus constitute a hierarchy of scales. Biological surfaces have adapted at different hierarchy levels for certain functionalities, such as non-wetting, low friction or high adhesion, and their surface roughness also involves a hierarchy of scales. The two hierarchies correlate with each other.

Among the most promising application of biomimetic surfaces are modern areas of nanotechnology, energy conversion and environment-friendly (‘green’) engineering. As biological systems involve molecular mechanisms, they provide inspiration for miniaturization of engineering applications and creating small and even molecular-scale engineering mechanisms. Biological molecules such as DNA, RNA, proteins and enzymes have an ability for molecular assembly and self-assembly, energy conversion, etc., so they present evidence that such operations at the molecular level can be achieved also by an engineer; thus, biomimetics has applications in the area of nanotechnology. Energy conversion and conservation can be another area of application, as surface effects involve
various modes of energy transition and dissipation. Self-cleaning surfaces also have potential for green engineering, as contamination with oil constitutes a serious environmental issue.

In this paper, we will review various biological surfaces adapted for high or low wetting, friction, adhesion and dissipation, with emphasis on their hierarchical structure. After that, we will study various aspects of the hierarchical structure of these surfaces. Since capillary effects are of great importance for micro- and nanoscale applications, we will then discuss the capillary effects associated with a hierarchical rough surface. After that, new potential applications will be discussed with the emphasis on energy and environmental (green) issues: new ways of energy conversion and self-cleaning.

2. Hierarchical structure in biological surfaces

Many functional biological surfaces have hierarchical structures that affect their adhesion, wetting and friction properties. These surfaces will be reviewed in the present section.

(a) Superhydrophobic plant leaves and the lotus effect

Leaves of many plants, which grow in extremely wet or extremely dry conditions, have developed the ability to repel or collect water. Scanning electron microscope (SEM) studies revealed that the hydrophobicity of the leaf surface is related to its microstructure (figure 1a). The main parameter that characterizes wetting is the contact angle (CA), $\theta$, under which the liquid surface comes in contact with the solid surface. If the solid has a water CA in the range $0^\circ < \theta \leq 90^\circ$, it is considered hydrophilic, while solids with $90^\circ < \theta \leq 180^\circ$ are considered hydrophobic. In a similar manner, surfaces that attract or repel oil and organic liquids are called oleophilic or oleophobic. Superhydrophobicity is defined as $150^\circ < \theta \leq 180^\circ$; in addition, superhydrophobic surfaces usually have low CA hysteresis, which is the difference between the advancing CA (at the front of the drop) and receding CA (at the back of the drop) on a tilted surface (figure 1b). Various definitions of CA hysteresis and experimental techniques to measure it are discussed by Bormashenko et al. (2008a). Surface roughness usually enhances hydrophobicity or hydrophilicity, so, to achieve superhydrophobicity, a plant leaf should have (i) a hydrophobic coating (usually wax) and (ii) surface roughness. A critical issue for superhydrophobicity is the formation of a stable composite interface with air pockets between the solid and water.

All primary parts of plants are covered by a cuticle composed of soluble lipids embedded in a polyester matrix, which makes the cuticle hydrophobic in most cases (Barthlott & Neinhuis 1997). The hydrophobicity of the leaves is related to another important effect, the ability of the hydrophobic leaves to remain clean after being immersed into dirty water, known as self-cleaning. This ability is best known for the lotus ($Nelumbo nucifera$) leaf that is considered by some oriental cultures as ‘sacred’ due to its purity. Not surprisingly, the ability of lotus-like surfaces for self-cleaning and water repellency was dubbed the ‘lotus effect’.

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The outer single-layered group of cells covering a plant, especially the leaf and young tissues, is called the epidermis. The protective waxy covering produced by the epidermal cells of leaves is called the cuticle. The cuticle is composed of an insoluble cuticular membrane covered with epicuticular waxes, which are mixtures of hydrophobic aliphatic components and hydrocarbons with chain

Figure 1. (a(i) and (ii)) Scanning electron microscope (SEM) image of a lotus leaf showing hierarchical structure: microscopic bumps (papillae) with submicron roughness. (b) A water drop on a tilted surface, exhibiting the advancing and receding CA (Nosonovsky & Bhushan 2007a).

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lengths typically in the range C16–C36, such as paraffins (Baker 1982). The SEM study reveals that the lotus leaf surface is covered by ‘bumps’, or, more exactly, built by papillose epidermal cells, often called papillae, which, in turn, are covered by an additional layer of epicuticular waxes (Barthlott & Neinhuis 1997). The wax is hydrophobic with a water CA of approximately 95–110°, whereas the papillae provide the tool to magnify the CA. The experimental values of the static water CA with the lotus leaf were reported as approximately 160° (Barthlott & Neinhuis 1997).

Neinhuis & Barthlott (1997) systematically studied the surfaces and wetting properties of approximately 200 water-repellent plants. They reported several types of epidermal relieves and epicuticular wax crystals. Among the epidermal relief features are the papillose epidermal cells. Either every epidermal cell can form a single papilla, or a cell can be divided into several papillae. The scale of the epidermal relief ranged from 5 μm in multipapillae cells to 100 μm in large epidermal cells. Some surfaces also were convex (rather than having real papillae) and/or had hairs (trichomes). Hairs may be built by multicellular structures (Koch et al. 2009). Wagner et al. (2003) also found various types and shapes of wax crystals at the surface. Interestingly, the hairy surfaces without wax, being subjected to rain, exhibited water repellency for short periods (minutes), after which water penetrated under the hairs, whereas waxy trichomes led to strong water repellency. The wax crystal surface is very rough, in addition to the roughness created by the papillae, and thus the submicron-scaled wax roughness is overimposed on the microscale papillae, creating a hierarchical structure. Apparently, roughness plays the dominant role in the lotus effect since superhydrophobicity can be achieved independently of the type of wax or other hydrophobic coating.

While it is intuitive that water repellency and self-cleaning are related to each other, because the ability to repel water is related to the ability to repel contaminants, a qualitative explanation of how was proposed by Barthlott & Neinhuis (1997), who suggested that, on a smooth surface, contamination particles are mainly redistributed by a water droplet; whereas, on a rough surface, they adhere to the droplet and are removed from the leaves when the droplet rolls off.

As far as biological implications of the lotus effect, Barthlott & Neinhuis (1997) suggested that self-cleaning plays an important role in the defence against pathogens, such as spores and conidia of pathogenic micro-organisms, as the growth of most pathogen micro-organisms, including bacteria and fungi, is limited by water shortage. Dryness is also beneficial for plant metabolism, since the uptake of CO₂ for photosynthesis is reduced on wet leaves where a liquid water film exists because CO₂ diffuses 10 000 times more slowly through water than air (Brewer et al. 1991).

(b) Gecko effect

Several creatures, including insects, spiders and lizards, have a unique ability to cling to and detach from walls using their attachment systems. Although these creatures have different foot morphology, in most cases they have small hairs that cover the surfaces of their feet, called setae. Using setae, animals develop close contact with a substrate that provides enough attachment force to clinging to...
and crawl on a wide range of natural and artificial surfaces. It also provides reversible adhesion, since they retain the ability to remove their feet from the attachment surface at will by peeling. This universal ability for attachment and detachment is called ‘smart adhesion’ (Bhushan et al. 2006; Kim & Bhushan 2007). The most advanced attachment ability is found in the Tokay gecko or Gekko gecko. This ability was known even in ancient times; almost 2500 years ago, the ability of geckos ‘to run up and down a tree in any way even with the head downwards’ was observed by Aristotle (Bhushan 2007). However, little was understood about the mechanism of this phenomenon until microscopic hairs covering the gecko’s toe were discovered in the late nineteenth century. The further investigation of the hierarchical morphology of gecko toe was conducted after the advent of the SEM in the 1950s (Gao et al. 2005).

The attachment pads of a gecko’s foot consist of a complicated hierarchy of structures beginning with lamellae, soft ridges approximately 1–2 mm in length located on the attachment pads (toes). Tiny curved hairs (setae) extend from the lamellae. These setae are typically 30–130 μm in length and 5–10 μm in diameter. The setae of a gecko have several branches. Each seta branches into several hundred substructures, called spatulae. A branched seta looks like a broom and has a length of approximately 20–30 μm and a diameter of approximately 1–2 μm. The tips of the spatulae have a typical size of the order of 500 nm in length, 200–300 nm in width and approximately 10 nm in thickness. Spatulae are oriented at an angle with respect to the contacting surface to facilitate peeling (Bhushan et al. 2006). Some attachment systems in other creatures, including insects and spiders, have similar structure to that of gecko feet. As the mass of the creature increases, the radius of the terminal attachment element decreases. This allows a greater number of setae to be packeted in an area (Bhushan 2007).

The adhesion force of a single seta was measured out by Autumn et al. (2000). The attachment pads of a T. gekko have a total area of two feet of the order of 200 mm², which can produce a clinging ability of approximately 20 N (vertical force required to pull a lizard down from a nearly vertical surface). In isolated gecko setae, a 2.5 mN preload yielded adhesion of 20–40 mN and thus an adhesion coefficient, which represents the strength of adhesion with respect to preload, was approximately 8–16. With regard to the natural living conditions of the animals, we can separate the mechanics of gecko attachment into two parts: the mechanics of adhesion of a single contact with a flat surface and an adaptation of a large number of spatulae to a natural rough surface (Bhushan et al. 2006; Kim & Bhushan 2007).

(c) Fish scale and underwater superoleophobicity

Fish scale is of interest for biomimetics for several reasons. For example, unlike sea birds, fishes are known to be well protected from contamination by oil pollution. Liu et al. (2009) suggested that underwater oleophobicity of fish scales is related to their hierarchical structure, consisting of sector-like fish scales (4–5 mm) covered by papillae (30–300 μm) with nanostructures upon them. This complicated structure can lead to water or air retention that can protect from marine fouling and play a role in defence against adhesion and growth of marine organisms, e.g. bacteria and algae. The usage of superhydrophobicity for
marine antifouling has been suggested earlier (Genzer & Efimenko 2006; Koch et al. 2009), as well as the biomimetic approach to antifouling coatings (Chambers et al. 2006).

Another possibility is the formation of a thin water layer that protects from oil contamination (Liu et al. 2009). In many cases, an oleophilic surface in air (solid–oil–air system) becomes oleophobic in water (solid–oil–water system). The CA with water, oil in air and oil in water is given by the Young equation as

\[
\cos \theta_W = \frac{\gamma_{SA} - \gamma_{SW}}{\gamma_{WA}}, \quad \cos \theta_O = \frac{\gamma_{SA} - \gamma_{SO}}{\gamma_{OA}}, \quad \cos \theta_{OW} = \frac{\gamma_{SW} - \gamma_{SO}}{\gamma_{OW}},
\]

(2.1)

where \( \gamma \) is the interface free energy and the indices stand for solid (S), water (W), oil (O) and air (A). Thus, for a hydrophilic material (\( \gamma_{SW} < \gamma_{SA} \)), an oleophilic material in air (\( \gamma_{SO} < \gamma_{SA} \)) can switch into an oleophobic material under water (\( \gamma_{SO} > \gamma_{SW} \)). As a result, oil contaminants are washed away when immersed in water. This effect leads to underwater oleophobicity and self-cleaning that can be used against marine ship fouling.

Another effect is associated with shark skin (Wainwright et al. 1978). The shark skin is covered by a special type of scales, called placoid, which form small V-shaped bumps, made from the same material as sharks’ teeth. The rough surface reduces friction when the shark glides through water, which makes sharks very quick and efficient swimmers. The shark skin is so rough that it can be used as sanding paper. The ‘shark skin effect’ is based on the fact that a body in a stream is provided with small ridges aligned in the local flow direction; a significant drag reduction can be reached in turbulent flow conditions owing to the control of the streamwise vortices in the turbulent flow (Nosonovsky & Bhushan 2008a).

(d) Pond skater

A pond skater (Gerris remigis) has the ability to walk upon a water surface without getting wet. Even the impact of rain droplets with a size greater than the strider’s size does not make it immerse into water. Gao & Jiang (2004) showed that the special hierarchical structure of strider legs, which are covered by large numbers of oriented tiny hairs (microsetae) with fine nanogrooves, may be responsible for the water resistance. According to their measurements, a leg does not pierce the water surface until a dimple of 4.38 mm depth is formed. They found that the maximal supporting force of a single leg is 1.52 mN or approximately 15 times the total body weight of the insect. The corresponding volume of water ejected is roughly 300 times that of the leg itself. Gao & Jiang (2004) suggested that superhydrophobicity of the pond skater leg is responsible for these abilities. They measured the CA of the insect’s legs with water and found it equal to 167.6°. Scanning electronic micrographs revealed numerous oriented setae on the legs. The setae are needle-shaped hairs with diameters ranging from 3 \( \mu \)m down to several 100 nm. Most setae are roughly 50 \( \mu \)m in length and arranged at an inclined angle of approximately 20° from the surface of the leg. Many elaborate nanoscale grooves were found on each microseta, and these form a unique hierarchical structure. This hierarchical micro- and nano-structuring on the leg’s surface seems to be responsible for its water resistance and the strong supporting force.

Phil. Trans. R. Soc. A (2009)
(e) Bird feathers

The dove’s feather constitutes another example of a natural superhydrophobic surface with a complicated structure (Bormashenko et al. 2007), namely a network formed by keratin-built barbs and barbules. The Biblical patriarch Noah sent a dove in order to discover whether the Earth had become dry after the flood, and the bird returned safely to the ark. The dove does not get wet from surrounding water due to the unusual properties of its feather (pennae). A drop deposited on the thoroughly cleansed feather vanes demonstrated obtuse apparent CAs as high as 140–150° (Bormashenko et al. 2007). The values of the CA are consistent with those predicted by the Cassie model with air trapped at the interface. The hierarchical twofold structure of the dove’s feather is noteworthy.

(f) Other surface effects

The moth eye effect is the ability of nanostructured optical surfaces to not reflect light; that is, to remain invisible. For nocturnal insects, it is important not to reflect the moonlight, since the reflection makes the insect vulnerable to predators. Light reflection is avoided by a continuously increasing refractive index of the optical medium. The little protuberances upon the cornea surface increase the refractive index. These protuberances are very small microtrichia (approx. 200 nm in diameter). For an increase in transmission and reduced reflection, a continuous matching of the refraction index at the boundary of the adjacent materials (cornea and air) is required. If the periodicity of the surface pattern is smaller than the light wavelength, the light is not reflected (Gorb 2006). For protuberances with 220 nm depth and the same spacing (typical values for the moth eye), a very low reflectance is expected for the wavelengths between 440 and 550 nm (Wilson & Hutley 1982). It is possible to also create transparent surfaces using the moth eye effect (Clapham & Hutley 1973). The moth eye effect involves surface roughness; therefore, it can be combined with the lotus effect, so that self-cleaning non-reflective glass can be obtained. Owing to the recent developments in nanophotonics and plasmonics physics, it became possible to manipulate light at the nanoscale using arrays of nanoparticles (Sukharev & Siedman 2007). The plasmonic nanodevices are designed for phase, polarization and feedback control, which allow them to guide light in the nanoscale via nanoparticle arrays. The moth eye effect may be viewed as the inspiration for these devices with the particles forming the moth eye structure to prevent reflection.

Many insects, such as butterflies, also use structural coloration owing to the presence of scales and bristles. Scales of the scarab beetles bear additional microtrichia responsible for the coloration of their surfaces, which serves for camouflage, mimicry, species and sex recognition. Some insects use a mechanism called iridescence, using a complex multilayer structure for optical interference. Such structures can produce complicated optical effects including strong polarization, colour mixing and reflection angle broadening (Gorb 2006). It has been suggested that this effect could be used for displays of various devices, such as cell phones, with a pixel composed of a MEMS gap-closing actuator that opens for half wavelength, calling the principle the ‘interference modulation (IMod)’. Unlike conventional displays that require an internal source of light and become
bleak in bright light (e.g. in the sunlight), the IMod displays work from reflected light and are seen well in the sunlight, consuming little energy. It is questionable, however, whether this effect constitutes a true biomimetic borrowing or just a similarity of a biological and a technical system.

The desert ‘sand fish’ skink (Scincus scincus) is the lizard that adapted to an underground existence and can virtually dive and ‘swim’ beneath the surface of loose sand owing to the special properties of its scales having very low friction and abrasion. The scale of the skink is covered by ‘nanothresholds’, long ridges with submicron height and distance of 10 μm or less. Rechenberg & El Khyeri (2007), who brought attention to this lizard and to what they call the ‘sand fish effect’, suggested that an electrostatic charge created by submicron-sized thresholds on the scale plays a role in friction reduction by creating a repulsive force between the scale and sand grains.

3. The effects of hierarchical surface structures

In this section, the effect of hierarchically organized surface structures on various properties, such as adhesion, wetting and friction, is discussed. First, we study the relation of the hierarchical structure with dissipation mechanisms having various characteristic scale lengths. The situation when an addition of small-scale surface roughness results in a significant change of properties, in particular those related to the stability, will be discussed next, as well as various theories of why many natural surfaces are hierarchical.

(a) Hierarchical structure and dissipation mechanisms

Structure–property relationships constitute the central topic of materials science. In order to develop a material with needed properties, it is necessary to control its hierarchical structure. In the case of biological surfaces, we deal with the hierarchical structures and, on the other hand, with the hierarchical organization of dissipation mechanisms. Thus, we have two types of hierarchies that are related to each other (figure 2). The difference between fabricated objects and grown biological objects is that the latter are formed by recursive algorithms rather than specifications and blueprints. As a result, biological systems provide a hierarchical structure that can adapt to various functionalities involving mechanisms of various characteristic length scales. Recursive algorithms also provide mechanisms of adaptive optimization at various scale levels, adaptation to environment and external influences and mechanisms of self-repair in the case of damage.
Hierarchical structures are characterized by a set of typical scale lengths at various levels, $l_1 < l_2 < \cdots < l_n$, which correspond to different levels of the structure. For example, in the case of the gecko toe, $l_{\text{spatulae}} = 20 \text{ µm}$, $l_{\text{setae}} = (30–120) \text{ µm}$ and $l_{\text{lamellae}} = 1 \text{ mm}$. A similar structure can be found in other biological surfaces considered in the previous section (table 2). An important class of hierarchical systems related to recursive algorithms are the fractal objects. The so-called self-similar or fractal structures can be divided by parts, each of which is a reduced-size copy of the whole. Unusual properties of the self-similar curves and surfaces, including their non-integer dimensions, were studied by mathematicians in 1930s. The word ‘fractal’ was coined in the 1970s by Benoit Mandelbrot, who popularized the concept of self-similarity and showed that fractal geometry is universal in nature and engineering applications (Mandelbrot 1983). The fractal concepts were applied to rough surfaces. In the late 1980s–early 1990s, the fractal geometry approach was introduced into the study of engineering rough surfaces (Majumdar & Bhushan 1990). The difference between a fractal surface and a hierarchical surface is that a fractal surface has no characteristic length scale, while a hierarchical surface has a set of characteristic lengths corresponding to various scale levels.

Various mechanisms of dissipation also have different characteristic scale lengths. Both friction and adhesion are complicated phenomena that involve physical mechanisms of different natures. Solid–solid friction depends on adhesion, elastic and plastic deformation and fracture. Adhesion includes van der Waals, chemical and capillary forces. While the chemical and van der Waals forces have length constants of a molecular scale, the capillary force exists due to water vapour condensation, and it has a characteristic scale called the capillary length, $l_c = (\gamma_{\text{LA}}/\rho g)^{1/2}$. For water at room temperature, $\gamma_{\text{WA}} \approx 0.072 \text{ N m}^{-1}$, $\rho \approx 1000 \text{ kg m}^{-3}$ and $l_c \approx 2.7 \text{ mm}$. Surface roughness parameters of the substrate are also important during the contact. For a random rough Gaussian surface, the main single parameters are the correlation length $\beta^*$ that characterizes the length

| Surface       | Structure and order of size                   | Function               |
|---------------|-----------------------------------------------|------------------------|
| lotus leaf    | papillae approximately $10 \mu m$             | contact area           |
|               | wax crystals more than $1 \mu m$              | air retention          |
| gecko toe     | lamellae approximately $1 \text{ mm}$         | structural strength    |
|               | setae approximately $100 \mu m$               | adaptation to large contact area |
|               | spatulae approximately $300 \text{ nm}$       | adaptation to large contact area |
| fish scale    | scale approximately $5 \text{ mm}$            | structural strength    |
|               | papillae approximately $100 \mu m$            | contact area           |
| pond skater   | setae approximately $50 \mu m$                | structural strength    |
|               | nanostructure approximately $100 \text{ nm}$  | water retention        |
|               | nanogrooves approximately $100 \text{ nm}$    | air retention          |
| bird (dove) feather | barbs                                      | structural strength    |
|               | barbules                                      | air retention          |
| sand skink    | scales approximately $1 \text{ mm}$           | structural strength    |
|               | nanothresholds approximately $100 \text{ nm}$ | electrostatic repulsion |
over which a random correlation decays (a typical length of an asperity) and the
standard deviation of surface height $\sigma$ (a typical height of an asperity). More
complicated surface roughness can lead to additional length parameters. Wetting
depends on interactions in the bulk of liquid volume, at the solid–liquid interface
and at the triple line. Corresponding interactions involve various mechanisms
(e.g. precursor and liquid layer formation) with length parameters at various
scale levels. The transition from the often unstable composite to homogeneous
interface is also an important effect governed by nanoscale interactions
(Nosonovsky & Bhushan 2007a).

(b) Cross-scale linking: when small roughness has a large effect

When contact problems are investigated, it is often assumed that the
contacting surfaces are smooth, because the introduction of surface roughness
with small amplitude is usually not expected to change the solution significantly.
The standard theories that combine contact mechanics and adhesion, such as the
Johnson–Kendall–Roberts (JKR) and Derjaguin–Muller–Toporov (DMT)
models, have been formulated for smooth surfaces (Adams & Nosonovsky
2000). Although real surfaces are rough, it is assumed that the introduction of
roughness yields only small corrections to the results. However, this assumption
is not always justified. Small roughness superimposed on a smooth surface can
lead to significant qualitative changes of the behaviour of the system under
investigation. Instead of a single energy minimum state, multiple minimums
separated by energy barriers can emerge. The schematic in figure 3a shows the
energy of a water drop as a function of the CA for a homogeneous (Wenzel) and
composite (Cassie) interface. For a smooth energy profile, there is only one
minimum that corresponds to the stable value of the CA. As soon as a small-scale
perturbation is imposed, e.g. due to surface roughness or heterogeneity, multiple
equilibriums emerge. Therefore, instead of a unique equilibrium state, a
spectrum of equilibriums emerges, including some metastable states. During
wetting, this mechanism leads to CA hysteresis, when the CA can have any value
between the advancing and receding CA values (Nosonovsky & Bhushan 2007c,
2008c). The hysteresis leads to dissipation and irreversibility of the wetting cycle,
so the introduction of roughness changes behaviour qualitatively from reversible
to irreversible. Small imperfection leads to dissipation, and this constitutes an
example of cross-scale linking.

The introduction of small-scale roughness may create new energy minimums,
and thus new equilibrium states, where a smooth surface has no equilibriums.
Nosonovsky (2007a) investigated the effect of nanoroughness upon a micro-
patterned hydrophilic surface (figure 3b). It was found that, for a convex
nanoroughness, new energy minimums emerge, and thus nanoroughness can pin
the triple line, preventing spreading of liquid and enhancing the stability of the
composite interface. For nanoroughness with a concave geometry, the
equilibriums are unstable and no pinning occurs (Nosonovsky 2007a).

For the capillary effects, introduction of a small roughness detail may lead to a
significant change of the shape of water meniscus and, therefore, of the meniscus
force. A small roughness detail can pin the meniscus far away from its position in
the absence of the roughness detail. An AFM experiment with a small rough
glass sphere (radius of 10 $\mu$m) shows that the capillary adhesion force changes
very significantly (400%) with a rotation of the sphere for a small angle (Yang et al. 2008a). These instabilities are of importance for capillary effects combined with the mechanical contact of elastic bodies (figure 3c).

Another situation involving cross-scale linking is related to the dynamic behaviour. Frictional stick-slip motion and liquid spreading are examples of ‘avalanche’-like behaviour, when a small input into the system leads to a big change. For example, a droplet on an inclined surface starts its motion when the tilt angle exceeds a certain critical value, so that the gradient of gravity exceeds the energy barriers associated with pinning of the triple line (figure 3d). Normally, the wetted and the dry states correspond to energy minima with a barrier between them. However, as the tilt angle grows, the gradient of the potential energy owing to the gravity grows as well, and at a certain moment the energy barrier disappears. That moment corresponds to the initiation of liquid spreading and can be viewed as a ‘critical state’ in the sense that the barrier between two states (dry and wet) disappears. This behaviour is referred to as ‘self-organized criticality’ (SOC). This behaviour is typical for both dry friction and wetting (Nosonovsky 2007b). Note that the scale of the avalanche is much greater than the scale of the initial perturbation; thus, the avalanche belongs to the upper level of hierarchical organization (Zypman et al. 2003; Nosonovsky & Bhushan 2008b; M. Nosonovsky 2008, unpublished). Conventional systems have phase states separated by energy barriers. At the critical point of a phase diagram the barrier between phase states vanishes. Many conventional physical systems that are studied at equilibrium have a critical point; that is, a point at which a distinction between two phases vanishes and a typical length of fluctuations (referred as the correlation length) tends to grow up to infinity. The systems with SOC have a critical point as an attractor, so that they spontaneously reach the vicinity of the critical point and exhibit power-law scaling behaviour.

This is illustrated in figure 3e, which shows the energy profile \( E \) of a symmetric nonlinear system characterized by a parameter \( x \), \( E = \alpha x^2 + \beta x^4 \). For \( \alpha > 0 \) and \( \beta > 0 \), the system has a stable equilibrium at \( x = 0 \), whereas, for \( \alpha < 0 \) and \( \beta > 0 \), the equilibrium at \( x = 0 \) is unstable and two additional stable equilibriums exist at \( x = \pm \sqrt{\alpha/(2\beta)} \), marked A and B. When stable equilibrium is destabilized due to decreasing \( \alpha \), the system is transferred from a symmetric to an asymmetric state. The critical state corresponds to \( \alpha = 0 \).

To summarize, small imperfections or roughness at the nano-/microscale level can lead to significant macroscale effects, such as irreversibility and dissipation. For example, CA is the macroscale parameter that characterizes wetting. However, due to nano-/microscale effects, CA hysteresis exists so that there is no single macroscale CA value. Addition of nano-/microscale roughness can also affect the stability of the macroscale parameters. Complicated physics at a lower scale level yielding the stable/unstable dichotomy or switching between equilibrium states at a higher level of hierarchy is a typical situation in systems with hierarchical organization.

(c) Role of hierarchy in biological surfaces

Hierarchical material structure is often used when a compromise between conflicting requirements is needed. For example, a tree should be high but at the same time light, and the compromise between these two requirements is achieved.
by introducing hierarchy (Fratzl & Weinkamer 2007). In the case of most biomimetic surfaces, hierarchical organization is the response to multiscale mechanisms of friction, adhesion and wetting and the need to deal with a large

Figure 3. Small-scale roughness can have a large effect on the properties (a) when roughness is superimposed on a smooth energy profile, it creates multiple states of equilibrium (Nosonovsky & Bhushan 2007c). (b(i) and (ii)) Small-scale convex details upon larger scale pillars can pin the triple line (Nosonovsky 2007a). (c(i)–(ii)) A small roughness detail can pin water meniscus and change significantly the meniscus force (Nosonovsky & Bhushan 2008f). (d) As the tilt angle $\alpha$, the critical state can be reached with disappearing energy barrier, so that the liquid advances (Nosonovsky 2009). (e) Changing the parameter $\alpha$ for the energy profile $E=\alpha x^2+\beta x^4$ results in the loss of symmetry (Nosonovsky & Bhushan 2007a).
range of conditions (e.g. micro- to macrodroplets in the case of the lotus effect or various scales of substrate roughness in the case of gecko toe).

The role of surface hierarchy in the lotus leaf remains not completely clear, although a number of explanations as to why most natural surfaces are hierarchical have been suggested (Herminghaus 2000; de Gennes et al. 2003; Lafuma & Quéré 2003; Patankar 2004; Bormashenko et al. 2006; Gao & McCarthy 2006; Nosonovsky 2007a; Nosonovsky & Bhushan 2007a,b). The CA with a hierarchical surface depends only slightly on the CA given by the Young equation (Bormashenko et al. 2008b). Nosonovsky (2007a) showed that the introduction of small-scale roughness enhances the stability of the composite (solid–liquid–air) interface, as convex roughness leads to stability and can prevent the triple line from propagation, while concave roughness leads to

*Phil. Trans. R. Soc. A* (2009)
instability. Nosonovsky & Bhushan (2007a,b) suggested that the mechanisms involved in superhydrophobicity, such as liquid condensation and surface capillary waves, are scale dependent, and thus the roughness must be hierarchical in order to respond to these mechanisms. It may also have to do with the simple fact that the surface must be able to repel both macroscopic and microscopic droplets. Experiments with artificial fog (microdroplets) and artificial rain (large droplets) show that surfaces with only one scale of roughness repel rain droplets well; however, they cannot repel small fog droplets that are trapped in the valleys between the bumps (Fürtner et al. 2005). In a similar manner to air retention with the lotus leaf, the nanogrooves of the pond skater leg provide air retention, while nanoroughness of the fish scale can provide water retention for underwater oleophobicity and self-cleaning. Large-scale structures provide the structural strength of the system, while small-scale structures provided desired wetting properties. The function of the nanostructures is also in the reduction of the contact area between the leaf surface and adhering contaminants.

The hierarchical structure of the gecko toe surface involves the ability to adjust to a rough surface providing a large contact area of adhesion. Lamellae, setae and spatulae have various elastic constants providing a flexible mechanism to adjust to surface roughness. This is demonstrated in figure 4, which shows how the addition of small-scale elastic elements allows increasing contact area with the substrate. The hierarchical structure of the gecko toe also serves the self-cleaning.

To summarize, hierarchical biological surfaces have roughness details of various length-scales. Large-scale details affect the area of contact and can provide structural strength, while small-scale roughness serves for air and water retention as well as for adjustment to small drops or small details of surface roughness. Characteristic scale lengths of the capillary effects and various processes involved in wetting are very important, so, in the next section, we will consider wetting in detail.
4. Capillary effects associated with nanocontacts

In this section, we will discuss the equations that govern wetting and thermodynamic equilibrium of the liquid and vapour phases. The solid–liquid adhesion and multiscale effects related to wetting will be discussed.

(a) Equations governing the capillary effects

Atoms or molecules at the surface of a solid or liquid have fewer bonds with neighbouring atoms than those in the bulk. The energy is spent on breaking the bonds when a surface is created. As a result, the atoms at the surface have higher energy. This surface energy or surface tension, \( \gamma \), is measured in N m\(^{-1}\), and it is equal to the energy needed to create a surface with the unit area. For a curved surface, the energy depends on the radius of curvature, as, at a curved surface, atoms have fewer bonds on average than at a flat surface. The curvature dependence of the surface energy is characterized by the Tolman's length \( d \), normally of the molecular scale, so that the surface tension of a curved drop’s surface with the radius \( R \) is related to that of a flat surface by

\[
\gamma_{\text{curved}} = \gamma \left( 1 + \frac{2\delta}{R} \right). 
\]

In a similar manner, molecules at the edge have fewer bonds than those at the surface, which leads to the line tension \( \tau \) measured in J m\(^{-1}\). The line tension is related to the Tolman's length, as an edge with a small radius \( R \) yields excess energy \( \alpha R \times 2\delta / R \), where \( \alpha \) is the angle of the edge (figure 5). When divided by the circumference length of the edge \( \alpha R \), the line tension is

\[
\tau = 2\gamma\delta. 
\]

If a liquid droplet is placed on a solid surface, the liquid and solid surfaces come together under equilibrium at a characteristic angle called the static CA, \( \theta_0 \), given by the Young equation

\[
\cos \theta_0 = \frac{\gamma_{\text{SA}} - \gamma_{\text{SL}}}{\gamma_{\text{LA}}}, 
\]

where \( \gamma_{\text{SA}} \) and \( \gamma_{\text{SL}} \) are the surface energies of the solid against air and liquid, and \( \gamma_{\text{LA}} \) is the surface energy of liquid against air. Taking into account the contact
line effect, for a droplet with radius $R$ is given by $\cos \theta = \cos \theta_0 + 2\tau/(R\gamma_{LA})$, where $\tau$ is the contact line tension and $\theta_0$ is the value given by the Young equation (Boruvka & Neumann 1977).

For a rough or heterogeneous solid surface, effective values of $\gamma_{SA}$ and $\gamma_{SL}$ lead to effective values of $\cos \theta$. Thus, the CA with a rough surface is related to that with a flat surface by the Wenzel equation

$$\cos \theta = R_f \cos \theta_0, \quad (4.4)$$

where the non-dimensional surface roughness factor, $R_f > 1$, is equal to the ratio of the solid surface area to its flat projected area. While it is usually assumed that $R_f = \text{const}$, a varying roughness factor may be considered as well (Nosonovsky 2007c). In a similar manner, for a surface composed of two fractions, one with the fractional area $f_1$ and the CA $\theta_1$ and the other with $f_2$ and $\theta_2$, respectively (so that $f_1 + f_2 = 1$), the CA for the heterogeneous interface is given by the Cassie equation

$$\cos \theta = f_1 \cos \theta_1 + f_2 \cos \theta_2. \quad (4.5)$$

For the case of a composite interface (figure 6) consisting of the solid–liquid fraction ($f_1 = f_{SL}$, $\theta_1 = \theta_0$) and liquid–air fraction ($f_2 = f_{LA} = 1 - f_{SL}$, $\cos \theta_2 = 1$), equation (4.5), with account of equation (4.4), yields the Cassie–Baxter equation

$$\cos \theta = R_f f_{SL} \cos \theta_0 - 1 + f_{SL}. \quad (4.6)$$

(b) Which parameter characterizes solid–liquid adhesion?

The CA is a macroscale parameter characterizing wetting. However, hydrophobicity/philicity is dependent upon the adhesion of water molecules to the solid. There is an argument in the literature as to whether superhydrophobicity is adequately characterized only by a high CA and whether a surface can have a high CA but at the same time strong adhesion. Jin et al. (2005) suggested that a surface can be superhydrophobic and at the same time strongly adhesive to water. They even introduced the term ‘petal effect’ for a surface that has a high CA, but also a large CA hysteresis and strong adhesion to water. Li & Amirfazli (2007) argued that since ‘superhydrophobicity’ means a strong fear of water or lacking affinity to water, ‘the claim that a superhydrophobic surface also has a high adhesive force to water is contradictory’. In addition, there is an argument on how various definitions of the CA hysteresis
are related to each other (Krasovitski & Marmur 2004; Bormashenko et al. 2008). It may be useful also to see the transition between the Wenzel, Cassie and dry states as a phase transition (M. Nosonovsky 2008, unpublished).

It is generally believed that a superhydrophobic surface should have a high CA (more than 150°), which is a measure of wetting, and low CA hysteresis, which is a measure of dissipation, and the two measures are not related directly to each other (i.e. a high CA does not automatically lead to low CA hysteresis). Furthermore, there are different ways to measure CA hysteresis, such as tilting a droplet at an inclined plane, simply adding/removing liquid or subjecting a droplet to evaporation/condensation, and these methods may lead to different values.

In addition to high CA and low CA hysteresis, it may be reasonable in certain cases to add a third criterion of superhydrophobicity; that is, bouncing off a surface by a droplet that hits the surface as a measure of dynamic effects. There is evidence that the same energy barriers are relevant for both the Cassie–Baxter transition and bouncing (Nosonovsky & Bhushan 2008). Speaking roughly, the CA is a measure of the solid–liquid adhesion at the two-dimensional contact surface, while CA hysteresis is related to the interactions at the one-dimensional triple line, and bouncing-off properties also involve three-dimensional viscous interactions.

(c) Thermodynamic equilibrium

When a fluid drop or bubble of radius \( R \) expands for a small distance \( \Delta R \), the volume changes for \( \Delta V = 4\pi R^2 \Delta R \), and the surface area changes for \( \Delta A = 8\pi R \Delta R \). Equating the energy needed for creating the surface, \( \gamma_{LA} \Delta A \), with the work done by the pressure difference \( \Delta P \) inside and outside the bubble due to the volume expansion, \( \Delta P \Delta V \), yields \( \Delta P = 2\gamma_{LA}/R \). In the general case of a curved surface with the principal radii of curvature, \( R_1 \) and \( R_2 \), the pressure change through the surface is given by the Laplace equation

\[
\Delta P = \gamma_{LA} \left( \frac{1}{R_1} + \frac{1}{R_2} \right). \tag{4.7}
\]

One consequence of the Laplace equation is that a liquid surface has a constant mean curvature \( (1/R_1) + (1/R_2) \).

At the thermodynamic equilibrium, condensation and evaporation occur at the same rate, and \( \Delta P \) is dependent on the partial vapour pressure. For saturated vapour, the mean curvature of the liquid surface is zero at equilibrium. A convex interface \( (1/R_1) + (1/R_2) > 0 \) results in evaporation prevailing over condensation; this is why small droplets tend to evaporate, as convex interface molecules have higher energy. However, a concave interface \( (1/R_1) + (1/R_2) < 0 \) results in condensation of saturated vapour prevailing over evaporation. Since the condensation prevails, a concave interface may be in thermodynamic equilibrium with undersaturated vapour. This is why concave menisci tend to condense even when the relative humidity is less than 100 per cent.

The relation between the vapour pressure and meniscus curvature is given by the Kelvin model. The pressure drop of water with density \( \rho \) risen for the height \( h \) in a capillary tube is \( \Delta P = \rho gh \). Using the Laplace equation and the hydrostatic formula for vapour pressure \( P = P_0 \exp(-gh/RT) \), where \( R \) is the gas constant

Phel. Trans. R. Soc. A (2009)
and $T$ is the temperature, yields the Kelvin equation

$$\gamma_{LA} \left( \frac{1}{R_1} + \frac{1}{R_2} \right) = \rho R T \ln \frac{P}{P_0},$$

(4.8)

which relates the interface curvature at the thermodynamic equilibrium with the ratio of actual and saturated vapour pressure, $P/P_0$ (relative humidity). According to the Kelvin model, a concave meniscus with a negative curvature given by equation (4.8) may form at any relative humidity. An important example of such meniscus is in condensed water capillary bridges at nanocontacts, for example between an AFM tip and a sample. Pressure inside the bridges is significantly reduced compared with the ambient and may reach deeply negative values, as small volumes of water can withstand a significantly negative pressure (tensile stress), as was shown by Yang et al. (2008b) and a consequent discussion in the literature.

(d) _Multiscale effects (multiple equilibriums, hysteresis, layers and precursors)_

It is emphasized that the CA provided by equations (4.3)–(4.6) is a macroscale parameter, so it is sometimes called ‘the apparent contact angle’. The actual angle, under which the liquid–air interface comes in contact with the solid surface at the micro- and nanoscale, can be different. There are several reasons for that. First, water molecules tend to form a thin layer upon the surfaces of many materials. This is because of a long-distance van der Waals adhesion force that creates the so-called disjoining pressure (Derjaguin & Churaev 1974). This pressure is dependent upon the liquid layer thickness and may lead to the formation of stable thin films. In this case, the shape of the droplet near the triple line transforms gradually from the spherical surface into a precursor layer, and thus the nanoscale CA is much smaller than the apparent CA. In addition, adsorbed water monolayers and multilayers are common for many materials. Second, even carefully prepared atomically smooth surfaces exhibit certain roughness and chemical heterogeneity. Water tends to cover at first the hydrophilic spots with high surface energy and low CA (Checco et al. 2003). The tilt angle due to roughness can also contribute to the apparent CA. Third, the very concept of the static CA is not well defined. For practical purposes, the CA, which is formed after a droplet is gently placed upon a surface and stops propagating, is considered the static CA. However, depositing the droplet involves adding liquid while leaving it involves evaporation, so it is difficult to avoid dynamic effects. Fourth, for small droplets and curved triple lines, the effect of the contact line tension may be significant. Molecules at the surface of a liquid or solid phase have higher energy because they are bonded to fewer molecules than those in the bulk. This leads to surface tension and surface energy. In a similar manner, molecules at the convex surface and, especially at the edge, have fewer bonds than those at the surface, which leads to line tension and curvature dependence of the surface energy. The curvature effect becomes important when the radius of curvature is comparable with the Tolman’s length, normally of the molecular size. The triple line at the nanoscale can be curved so that the line tension effects become important, especially for droplets with a linear size below 100 nm (Pompe & Herminghaus 2000; Blecua et al. 2006).
The CA, taking into account the contact line effect, for a droplet with radius $R$ is given by \[ \cos \theta = \cos \theta_0 + 2\tau/(R\gamma_{LA}), \] where $\tau$ is the contact line tension and $\theta_0$ is the value given by the Young equation (Boruvka & Neumann 1977). Thus, while the CA is a convenient macroscale parameter, wetting is governed by interactions at the micro- and nanoscale, which determine the CA hysteresis and other wetting properties. Table 3 shows various scale levels that affect wetting of a superhydrophobic surface.

When only one scale level of surface geometry is considered, many surfaces are treated as smooth ones; for example, the AFM tip is treated usually as part of a sphere. However, real surfaces are usually not smooth. The ‘second-order’ roughness may cause effects that are very significant. For example, due to the presence of small-scale roughness, wetting hysteresis (CA hysteresis) exists as multiple equilibrium states are formed. A small change of roughness details may also cause a very significant change in the shape of the water meniscus.

5. New applications: optical surfaces, energy and underwater self-cleaning

Traditional applications of the lotus effect include self-cleaning paints, glass coatings and textiles. A number of emerging applications have been discussed in the literature, ranging from anti-bouncing additives for pesticides, to non-adhesive surfaces for microdevices, to microfluidics (Nosonovsky & Bhushan 2008a). In this section, we will discuss new potential applications for self-cleaning optical surfaces, energy conversion and conservation and environment-friendly self-cleaning underwater surfaces.

(a) Optical applications

The self-cleaning effect is particularly important for optical applications such as lenses and mirrors that have to stay clean. This is why a number of attempts have been made to design transparent, non-reflective and highly reflective superhydrophobic surfaces. In order for the surface to be transparent, roughness details should be smaller than the wavelength of the visible light (approx. 400–700 nm;
Nakajima et al. (1999). Teshima et al. (2005) obtained a transparent superhydrophobic surface from a polyethylene terephthalate (PET) substrate via selective oxygen plasma etching followed by plasma-enhanced chemical vapour deposition using tetramethylsilane (TMS) as the precursor. Attempts to create superhydrophobic surfaces by casting and nanoimprint methods have been successful. Yabu & Shimomura (2005) prepared a porous superhydrophobic transparent membrane by casting a fluorinated block polymer solution under a humid environment. The transparency was achieved because the honeycomb-patterned films had subwavelength pore size. Shang et al. (2005) did not blend low-surface energy materials in the sols, but described a procedure to make transparent superhydrophobic surfaces by modifying silica-based gel films with a fluorinated silane.

The superhydrophobic surfaces with high reflectivity might provide a promising self-cleaning approach in a wide variety of optical applications ranging from traffic to solar energy industries. However, the contradiction between the hierarchical micro-/nanostructure and the high reflectivity is a big challenge for superhydrophobic materials with high reflectivity. Silver mirror reaction has been and still is used in mirror and vacuum flask industries as an effective method for preparing high reflective surfaces. Shen et al. (2008) pointed out the contradiction between transparency and superhydrophobicity on their transparent superhydrophobic surfaces. The same contradiction between reflectivity and superhydrophobicity may exist. From the viewpoint of surface roughness, hydrophobicity increases when the surface roughness increases, while reflectivity decreases as the surface roughness increases. Shen et al. (2008) reported a facial method to fabricate a superhydrophobic silver film with reflectivity as high as polished silicon by carefully controlling a seed-induced silver mirror reaction.

(b) Oleophobicity and fuel economy

Another potential area of application is fuel economy using superoleophobic surfaces. Residual fuel in fuel tanks and pipes leads to significant losses of fuel, and thus it is desirable to use oleophobic surfaces. However, the surface tension of organic liquids is much lower than that of water, so it is extremely difficult to create a superoleophobic surface. Tuteja et al. (2008) suggested that, although creating such a surface would require a surface energy lower than that of any known material, surface curvature, in conjunction with chemical composition and roughened texture, can be used for liquids with low surface tension, including alkanes such as decane and octane. They used the curvature-dependent stability criteria suggested by Marmur (2003) and Nosonovsky (2007a) in order to design these surfaces.

(c) Energy conversion and capillary engines

The important area of application of superhydrophobic surfaces is reversible superhydrophobicity, that is, the ability of a surface to switch between the hydrophobic and hydrophilic properties under the influence of electric potential, ultraviolet or light irradiation or temperature. This area has emerged in recent years, since 2004, and a number of important findings have been made, including the ability to switch between the Cassie and Wenzel states. Krupenkin et al. (2007)
reported that droplet behaviour can be reversibly switched between the superhydrophobic Cassie state and the hydrophilic Wenzel state by the application of electrical voltage and current (electrowetting). Wang et al. (2007) created a surface that can switch between stable superhydrophilic, metastable superhydrophobic and stable superhydrophobic states. Interestingly, their reversible surface was driven by DNA nanodevices. A number of other approaches to reversible superhydrophobicity have been suggested as well.

The common feature of these mechanisms is that, by changing a controlling parameter (e.g. the temperature), the state of the system is transformed from hydrophobic to hydrophilic and vice versa. Potentially, these mechanisms can be used for new ways of energy conversion. When the steam engine was invented by James Watt in the eighteenth century, the principle that it used was to transform water into steam by boiling and then converting the pressure into mechanical energy. New applications, such as BioMEMS or lab-on-the-chip, require autonomous sources of energy.

A microscale capillary engine that uses reversible superhydrophobicity may be used for these devices. One possible scheme is presented in figure 7, showing a tip upon a solid substrate. The tip is held by an elastic spring (such as a cantilever). Increasing the surface energy to the value of $\gamma_0$, e.g. by applying an electric potential or light irradiation, leads to the formation of a capillary bridge, and the meniscus force deflects the tip. Decreasing the surface energy to the value of $\gamma_1$ results in the disappearance of the capillary bridge, and the tip is returned to its original position by a spring. The capillary force also depends nonlinearly on the separation distance between the tip and the substrate, and as soon as the capillary bridge is formed the tip can snap onto the surface. A similar principle is used for micro-object manipulation using a small droplet, as the droplet is picked up by a cantilever when the substrate has low energy and released when the substrate has high surface energy.

Figure 7. A ‘capillary engine’ that converts the change of the surface energy into the mechanical energy. (a) In the first state, the surface energy is high enough to form a meniscus, and the meniscus force deflects the tip. (b) In the second state, the surface energy is lower, the meniscus is destroyed and the tip is returned by the elastic force to its equilibrium position (Nosonovsky & Bhushan 2008e).
Another possible realization of this idea was suggested by S.-H. Yang, R. Gates, M. Nosonovsky & R. Cook (2007, private communication), who noted that a water capillary bridge between an AFM cantilever and a flat substrate evaporates when irradiated by a laser beam due to heating. The temperature rise due to the irradiation is lower than 100°C; however, due to its concave shape, the Laplace pressure inside the meniscus is small, and it can boil with a modest increase of the temperature above the ambient (figure 8). The bubbles that form and collapse cause the motion of the cantilever, and thus the heat is converted into mechanical energy similarly to a traditional steam engine, with the difference being that much lower temperature (e.g. human body temperature) can be used as the power source.

(d) Underwater applications

The ability of superhydrophobic surfaces to retain air when immersed in water leads to a number of potential applications. One area of application is related to the drag reduction of an underwater vessel (e.g. a submarine). The no-slip boundary condition that states that fluid velocity next to a solid surface is a standard assumption in hydrodynamic problems. It has been argued recently that slip may be present in many microfluidic systems, in particular owing to the
presence of an adsorbed layer of nanobubbles (Nosonovsky & Bhushan 2008a,f).

Since gas viscosity, \(\mu_G\), is much lower than liquid viscosity, \(\mu_L\), the air or vapour layer of thickness \(H\) leads to the apparent slip length

\[
l = H \left( \frac{\mu_L}{\mu_G} - 1 \right).
\]  \hspace{1cm} (5.1)

Liquid slip reduces resistance to flow very significantly. Roughness increases the ability of a surface to retain air and form the composite interface and thus reduces water friction with the walls of a channel (figure 9).

In addition to the drag reduction, a superhydrophobic surface can protect from marine fouling and play a role in defence against adhesion and growth of marine organisms (Genzer & Efimenko 2006). An air layer can form between a water droplet and a superhydrophobic surface. Underwater, in a similar manner, a water layer can form between an oil contaminant droplet and a superhydrophobic surface, as was explained above (equation (2.1) and following discussion). Underwater oleophobicity can lead to a similar effect in the case of contamination by organic liquids (figure 10). It is known that contamination, for example during oil spills, affects birds; however, fishes often remain untouched. It has been suggested (Liu et al. 2009) that fishes can resist pollution by organic contaminants in water due to the roughness of their scales, in a similar manner to the lotus leaf repelling water. Thus, a hydrophobic surface can become oleophobic and self-cleaning in water, as was explained in the preceding sections.

Figure 9. (a,b) Liquid flow upon a superhydrophobic surface. Air or vapour layer of thickness \(H\) leads to the apparent slip length \(l\) (Nosonovsky & Bhushan 2007b).

Figure 10. (a,b) Superhydrophobic surface with a composite interface can become superoleophobic when immersed under water. The effect can be used as an environment-friendly biomimetic tool to resist contamination and biofouling at the underwater parts of ships.
The effect can be used as an environment-friendly biomimetic approach to resist contamination and biofouling at the underwater parts of the ships (as opposed to toxic chemical coatings that repel marine organisms).

6. Conclusions

Biological surfaces achieve remarkable functional properties due to their hierarchical structure. This structure is a result of hierarchical organization of biological tissues, in general, that allows biological organisms to achieve adaptation and self-healing. The hierarchical organization provides the ability to adjust to energy dissipation and transition mechanisms that have various characteristic scale levels and are organized in a multiscale manner. For a macro-/microstructured surface, the addition of a lower scale (micro-/nanoscale) hierarchical level can change qualitatively the properties of the system, for example introducing multiple equilibriums, instability and dissipation. Thus, roughness with small details has a large effect. For example, a small change of surface roughness can lead to a large change in the capillary adhesion force. The capillary effects are particularly important for small-scale applications. The hierarchical structure of hierarchical surface and multiscale organization of the energy transition and dissipation mechanisms during adhesion, friction and wetting can be applied to new areas such as new ways of energy transition for nanotechnology application and environment-friendly technologies.

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