

Introduction

Abstract In the introduction chapter, the subjects and definitions of the surface science and tribology are discussed, as well as their relations to the concepts of hierarchy, mesoscale, energy dissipation and biomimetics.

1.1 Surfaces and Surface Free Energy

Surface science is defined as the study of physical and chemical phenomena that occur at the interface of two phases (solid–liquid, solid–gas, solid–vacuum) or of different substances of the same phase (solid–solid, liquid–liquid) [6]. Various properties of matter (e.g., the density, ρ) can change rapidly at the interface. It is therefore convenient to assume that the interface is a geometrically two-dimensional surface in a sense that every point at the interface can be characterized by only two parameters. In reality, every interface has a nonzero thickness and the bulk properties change gradually at the interface; however, the thickness is so small compared to the two other dimensions that it can often be neglected.

An important characteristic of every surface or interface is the surface free energy, γ . In the bulk of the body, chemical bonds exist between the molecules and certain energy has to be applied in order to break the bonds. The molecules that do not form the bonds have higher potential energy than those that form the bonds. Molecules at the surface do not form bonds at the side of the surface and thus they have higher energy. This additional energy is called surface or interface free energy and is measured in the energy per area units, that is, in the SI system, J/m^2 or N/m . In order to create an interface (e.g., to form a vapor bubble inside boiling water), the energy should be applied which is equal to the area of the interface multiplied by the interface free energy. For the stable existence of the interface it is required that the free energy of formation of the interface be positive, so that accidental fluctuations do not result in the dispersion of one material into the other. The opposite example of an interface, which does not offer opposition to the dispersion, is that between two gases or between miscible liquids [6]. Any system tends to achieve a position that

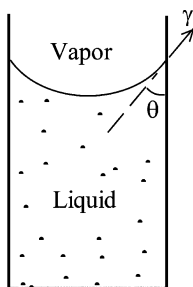


Fig. 1.1. Capillarity effect. Concave meniscus in a tube with water contact angle, θ , of less than 90° . The surface tension force

corresponds to a minimum energy. This is the reason why bubbles and droplets tend to have a spherical shape.

The concept of surface tension was introduced in 1805 by Thomas Young (1773–1829) and almost simultaneously by Pierre-Simon Laplace (1749–1827), while the idea of free surface energy was suggested by Josiah W. Gibbs (1839–1903) in about 1870, and it remains the foundation of the surface science. The accurate thermodynamic definition of the surface free energy involves a distinction between the concepts of the Gibbs free energy (the useful work obtainable from an isothermal isobaric thermodynamic system) and Helmholtz free energy (the useful work obtainable from a closed thermodynamic system). However, for processes that occur under constant pressure and temperature, the difference between these concepts is not significant, so in this book we will speak just about the surface free energy.

The obvious manifestation of the free surface energy is found in the capillarity effect (Fig. 1.1), defined as the ability of a substance to draw another substance into it [6, 283]. When the size of a liquid droplet or a channel is much smaller than the so-called capillary length, given by $l_c = (\gamma/\rho g)^{1/2}$ (where $g = 9.81 \text{ m/s}^2$ is the gravitational constant, γ is the free surface energy, and ρ is the density of liquid), the surface energy dominates over the gravity potential energy and the corresponding capillary forces dominate over the weight. The surface tension force is the force which should be applied to the solid–liquid–air contact line (the triple line) to expand the solid–liquid interface. The surface tension is measured in N/m and in many senses it is equivalent to surface free energy. For water at room temperature, $\gamma \approx 72 \text{ mN/m}$, $\rho \approx 1000 \text{ kg/m}^3$, and $l_c \approx 2.7 \text{ mm}$.

The interest in surface science is stimulated by the current advances in nanoscience and nanotechnology. Although the volume of a body is proportional to the third power of its linear size, the surface area is proportional to the second power of the linear size. With decreasing size of an object, the surface-to-volume ratio grows and surface effects dominate over the volume effects. This is why for small objects, all surface phenomena, such as capillarity, adhesion, friction, etc., become increasingly important.

1.2 Mesoscale

The length scale less than 1 mm but larger than 100 nm is considered microscale, and the length scale less than 100 nm but larger than the atomic scale is considered nanoscale [8, 36]. In a different manner, the scale length larger than the atomic scale (i.e., 1 nm or less) but smaller than the macroscale (i.e., between 1 nm and 1 mm) may be called mesoscale. There are several types of objects that are usually considered by physicists as mesoscale objects: systems that are of submicron size in at least one dimension, such as nanoparticles; soft condensed matter materials (foams, gels, polymer melts), which are characterized by a mesoscopic length scale; and systems in a near-critical state (near a phase transition point), which possess mesoscopic “correlation length” characterizing spontaneous fluctuations [8].

Nanoscale systems, even with a typical size of several nanometers, involve hundreds and thousands of molecules and can often be considered as a continuum system. However, many of their physical properties are different from macroscale bulk properties. For example, the yield strength and hardness are known to be higher when measured at the nanoscale compared to the macroscale values [42, 51, 159, 230]. The reason for that is believed to be the fact that a solid material consists of a large number of submicron-sized grains, domains, and defects. It is much easier to deform material when the size of the deformation is greater than the size of a grain. At the nanoscale, there are no such defects and material is much stronger. This effect is taken into account by strain-gradient plasticity theories [159, 230].

Another example of how properties at the nanoscale differ from those at the microscale is found in the phase transition, such as boiling/condensation and melting/freezing. At the macroscale, water is known to boil at 100 °C and to freeze at 0 °C; at the nanoscale, however, the situation may be quite different [346]. This is because in order to transform into a different phase, an interface should be created (e.g., a vapor bubble inside the bulk of liquid) which requires additional activation energy. In order to grow, however, the size of a bubble must be greater than a certain critical size, so at the nanoscale the bubble would not be formed. Furthermore, due to the capillary effects and small radii of curvature of nanodroplets and nanoscale water columns, the pressure inside water volumes (the so-called Laplace pressure) may be significantly different from the ambient, e.g., it may be negative (tensile strength) [249, 346].

Adhesion or molecular attraction between bodies in contact is a very important effect at the nanoscale. Adhesive force is a generic name for different forces that can pull together small bodies. Physically, the adhesion force involves the relatively weak and long-range (nanometers) van der Waals electric forces; the relatively strong and short-range chemical bonds between molecules, the electrostatic force; and the meniscus attractive force caused by condensed water bridges near the contacts.

Although many concepts of mesoscale physics and thermodynamics were developed a long time ago, only recently has a high degree of generality—originating from the existence of the mesoscale—been recognized. There are several universal methods that allow physicists to deal with the mesoscale. These methods include the

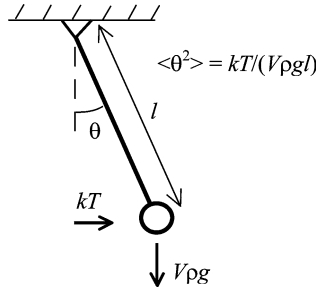


Fig. 1.2. Deflection of a nanoscale pendulum as a result of thermal fluctuations

renormalization group theory, scaling theory, Landau–Ginzburg mesoscopic functional, percolation, etc. [8].

A characteristic feature of mesoscale systems is that fluctuations, or spontaneous deviations from equilibrium, can play a significant role in them [8]. For example, consider a small microscale pendulum of length l with a mass $m = V\rho$ with its position characterized by the angle θ (Fig. 1.2). Collision with molecules results in the mean square position of the micropendulum being equal to

$$\theta^2 = kT/(V\rho g l), \quad (1.1)$$

where k is the Boltzmann constant and T is temperature. Thus, unlike the macroscale pendulum, the typical position of the micropendulum will be different from $\theta = 0$ due to the thermal random fluctuation.

The concept of mesoscale is closely related to the critical phenomena, i.e., phase transitions. Close to a critical point of any kind, the fluctuations become so large that they exhibit macroscale behavior [8]. Critical point is a point at the phase diagram where distinction between two phases vanishes. For example, the critical point of water is at around 374 °C and 218 atm, and the distinction between liquid and gas water at these conditions disappears. Asymptotically close to the critical point, the physical properties obey simple power laws, called the scaling laws. The physical basis for the scaling theories is in the divergence of a mesoscopic characteristic length scale known as the correlation length of the fluctuation. Powerful physical techniques, such as the renormalization-group theory and the Landau–Ginzburg functional, which were originally formulated for phase transition, have been proposed to calculate the critical exponents of the scaling laws and to study the near-critical behavior. The phase transition between a “disordered” and “ordered” state implies that an order-parameter can be identified, which is equal to zero for the disordered phase and different from zero for the ordered phase. Then, power exponents for the scaling laws can be determined. The phase transition approach has also been applied to the molecular-scale friction [104]. In solid mechanics, the common “phase transition” is that between the elastic and plastic phases. Modern theories of plasticity intended for the micron and submicron scale (the strain-gradient plasticity) postulate mesoscale length parameters, which result in the scale dependence of the yield strength and

hardness at the mesoscale [122, 159, 230]. The strain-gradient plasticity approach can be applied for the study of scale effect on friction [42].

1.3 Hierarchy

The concept of hierarchy is different from the concept of scale in that hierarchy implies a complicated structure and organization. Studying hierarchical systems often requires a multidisciplinary approach. Investigation of hierarchical surfaces involves mechanics, physics, chemistry, biochemistry, and biology. Hierarchical surfaces are built of elements of different characteristic length, organized in a certain manner (Fig. 1.3). This organization leads to certain functionality. Many examples of these surfaces are found in biology and will be considered in this book.

An important class of hierarchical systems 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 noninteger dimensions, were studied by mathematicians in 1930s. The word “fractal” was coined in 1975 by Benoit Mandelbrot, who popularized the concept of self-similarity and showed that fractal geometry is universal in nature and engineering applications [214]. The fractal concepts were applied to the rough surfaces. In the late 1980s and through the early 1990s, the fractal geometry approach was introduced into the study of engineering rough surfaces by Gagnepain and Roques-Carnes [119], Ling [205], Majumdar and Bhushan [212, 213], and others.

1.4 Dissipation

Many physical processes result in irreversible energy dissipation. Examples include plastic deformation, friction, and viscosity. The energy during dissipative process is converted into heat. The second law of thermodynamics, formulated by Rudolf Clausius (1822–1888), states that the heat, Q , cannot of itself pass from a colder to a hotter body. The mathematical formulation is that the entropy S , defined as $dS = dQ/T$, can only increase (for irreversible process) or remain constant (for reversible processes). When heat dQ is transformed from a system at temperature T_1 to that at T_2 , the change of entropy is $dQ(1/T_2 - 1/T_1)$, so the entropy grows when heat is transmitted from a hot to a cold body. The second law has a statistical nature and states that a system tends to transfer from a more ordered state to a less ordered state, which is statistically more probable. The state of thermodynamic equilibrium, at which the temperatures of the contacting bodies are equal ($T_1 = T_2$), corresponds to the less ordered, most probable state and to the highest entropy. At the nanoscale, when the typical energy of the system is comparable with kT , the second law can be violated due to small fluctuations, which can lead to local reductions of the entropy of the system [8].

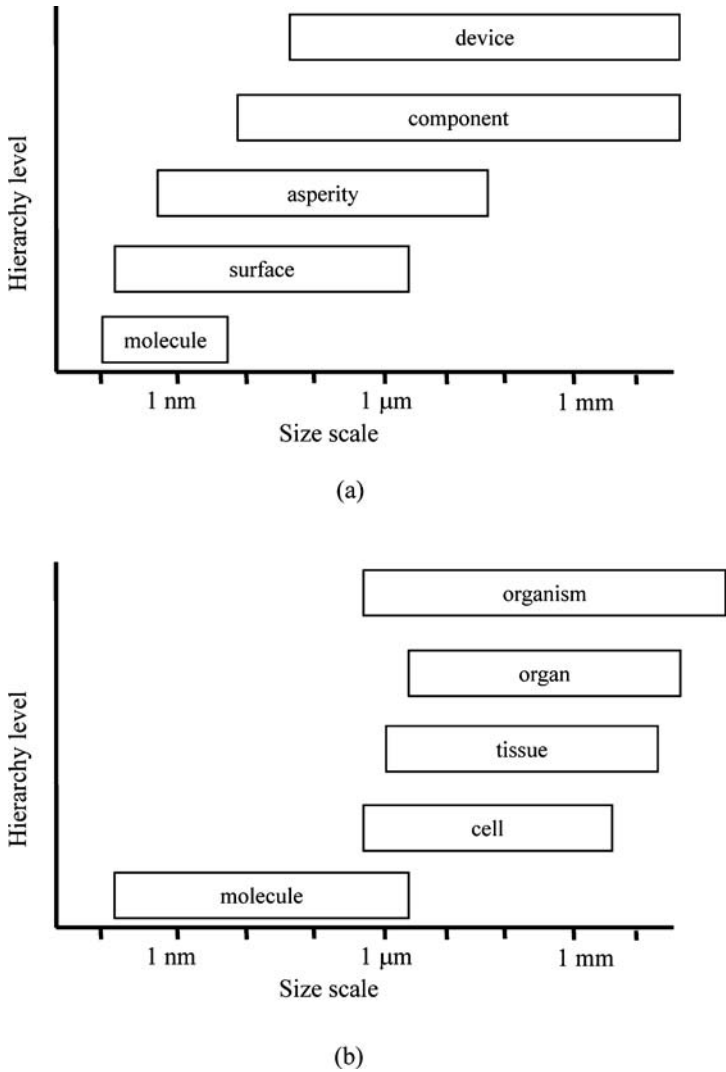


Fig. 1.3. Scale size and hierarchy levels in **a** engineering devices and **b** biological organisms [246]

Throughout this book we will deal with dissipative processes such as friction; however, our focus will be upon mechanical processes, which are usually slower than thermodynamic processes and thus in most cases we will assume that the system is at a thermodynamic equilibrium at a constant temperature T . In this case, the amount of dissipated energy is an appropriate measure of dissipation.

Classical thermodynamic systems, studied by Clausius, are characterized by an increasing disorder [6, 283]. Ilya Prigogine (1917–2003) and his students showed

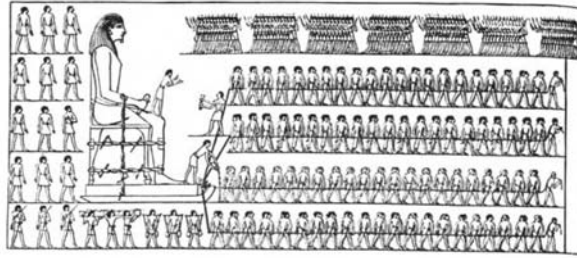
that some thermodynamic systems may lead to an increasing order and self-organization [271]. These so-called dissipative systems are thermodynamically open systems that operate far from thermodynamic equilibrium and can exchange energy, matter, and entropy with the environment. The dissipative systems are characterized by spontaneous symmetry breaking and formation of complex structures, where interacting particles exhibit long-range correlations. Examples of such systems are the Bénard cells in boiling liquid and oscillating chemical reactions. As in the case of the mesoscale thermodynamics, many of these systems were known a long time ago; however, the universality and generality of the processes involved in these systems was understood only through the works of Prigogine. It is believed that this ability for self-organization of physical systems led to the formation of complex hierarchical chemical and biological systems. Nonequilibrium dissipative systems may lead to the hierarchy, and their investigation involves the study of instability and asymmetry. Self-organization is related to an enormous reduction of degrees of freedom and entropy of the macroscopic system, consisting of many nonlinearly interacting subsystems, which macroscopically reveals an increase of order. The flow of heat, entropy, and material away from the interface during dry friction and wear can lead to self-organization so that the so-called “secondary structures” can form [113].

An important example of self-organization that was studied extensively by P. Bak [18] is the so-called “self-organized criticality,” which implies that a system can spontaneously achieve a critical-point-like behavior. The related broad field is embraces two disciplines: Complexity Science, where the systems under study are between the perfect order and complete randomness, and Synergetics, an interdisciplinary science that explains the formation and self-organization of patterns and structures in systems far from thermodynamic equilibrium. These disciplines employ theoretical concepts similar to those of the mesoscale physics, e.g. the Landau–Ginzburg functional and the order-parameter [141].

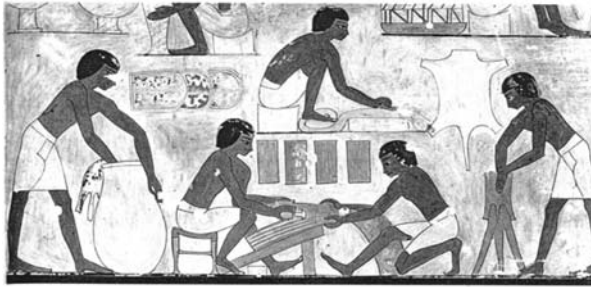
1.5 Tribology

Tribology is defined as the study of contacting surfaces in relative motion [30, 32]. As opposed to surface science, tribology is an application-oriented discipline, which studies adhesion, friction, lubrication, and wear, and involves mechanics, physics, chemistry, materials science, biology, and other related areas. The word “tribo-physics” (from the Greek word *tribos* “to rub”) was coined in the 1940s by David Tabor (1913–2005), who then worked in Australia [101]. The first official use of the term “tribology” was in 1966 in the British governmental report on research in this area (the so-called “Jost report”).

Although the word appeared only about 40 years ago, mankind has paid attention to friction and lubrication since ancient times. There is evidence that water lubrication was used in ancient Egypt as early as 2300 BC and 1800 BC, shown in two examples in Fig. 1.4. Oil lubrication is apparently mentioned in the Bible in the King Saul story (1020 BC), animal fat could be used as a lubricant for ancient Egyptian and Chinese chariots, and there is a list of lubricants in the treatise of Roman au-



(a)



(b)

Fig. 1.4. Tribological technology in the ancient world. **a** Painting from El-Bersheh, circa 1880 BC, showing transportation of a giant statue. Man in front of the statue pouring liquid from a jar. Some historians suggested that the liquid served ceremonial purposes, whereas some engineers suggested that this is one of the first recorded cases of lubrication [101]. **b** A tomb painting from Theba (Egypt) shows manufacturing of leather-covered shields, with finished shields appearing at the upper left (2nd millennium BC). The Bible mentions using olive oil lubrication for smoothening leather-covered shields in the end of the second millennium BC [236]

thor Pliny the Elder (1st century BC) [101, 236]. The emergence of modern study of friction and lubrication is related to the activity of Leonardo da Vinci (1452–1519), Guillaume Amontons (1663–1705), and Charles August Coulomb (1736–1806), who formulated empirical rules of friction (Fig. 1.5) [224].

Modern tribology concentrates on issues such as rough surface topography, contact mechanics, adhesion, mechanisms of dry and lubricated friction, hydrodynamic (thick film) and boundary (thin film) lubrication, bearings, lubricant chemistry and additives, wear, surface texturing, and medical and biotribology.

Since the 1990s the new field of nanotribology has emerged due to the advances of nanotechnology [31, 34–36, 50]. The idea of nanotechnology was suggested in 1960 by physicist Richard Feynman (1912–1985), who pointed out that there is a physical possibility for manufacturing very small devices, which would be able to perform many tasks considered earlier impossible. The field of nanotechnology emerged and began to grow in the 1990s, stimulated by such discoveries as carbon

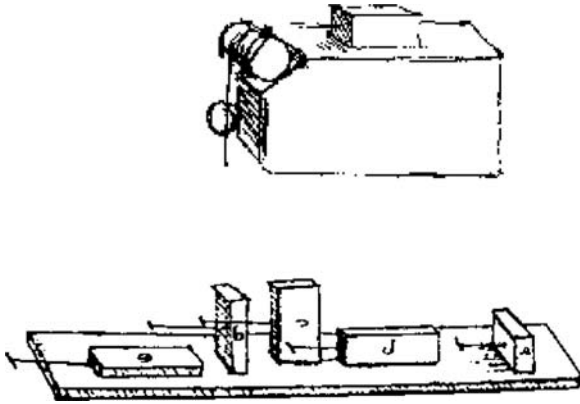


Fig. 1.5. Sketches by Leonardo da Vinci of his devices used to investigate friction laws [224]

nanotubes, C_{60} molecules (fullerenes), graphene (graphite monolayer), and quantum dots. Today it is one of the fastest growing research areas [36, 267]. Although presently the number of practical nanotechnological products is limited, according to some predictions the field may lead, in the next decade, to a technological revolution comparable with the one caused by the emergence of the transistor and microelectronics in the second half of the 20th century. However, right now nanoscience and nanotechnology remain an area of active fundamental and applied research. As it explained earlier, all kinds of surface effects are very important for small devices and therefore a significant part of the nanotechnological research is in nanotribology [38].

Nanotribology concentrates on the study of adhesion, friction, lubrication (in particular, by self-assembled molecular monolayers), and wear at the nanoscale [31, 34, 35, 50]. The main instrument currently employed for nanotribological research is the atomic force microscope (AFM) and its variations (friction force microscope and various other scanning probe microscopes). In the AFM, a small cantilever (typical length is $100\mu\text{m}$ or less) with a very sharp tip (typical radius is $10\text{--}30\text{ nm}$) can scan the surface of a sample, the position of which is controlled with great accuracy by a piezoelectric element. In contact with the surface or under the effect of forces (such as the adhesion force), the cantilever can bend and its deflection can be measured with a reflected laser beam. If the stiffness of the cantilever is known, it can be converted into the force acting upon the tip and thus small adhesion and friction force can be measured with high accuracy.

1.6 Biomimetics: From Engineering to Biology and Back

Biomimetics means mimicking biological objects in order to design artificial objects with desirable properties [25]. Another term used sometimes is bionics. The word was coined in the 1960s by biophysicist Otto Schmitt (1913–1998), though biologi-

cal objects have been actively studied by physicists and chemists before that. However, biomimetics goes further than just biophysics and bioengineering, which only study biological objects, since its objective is to imitate the objects' desirable properties. The idea behind biomimetics is that nature's technical solutions—achieved by millions of years of evolution (or, maybe, given by God, depending on scientist's personal convictions)—are perfect or at least better than those which contemporary engineering technology can suggest. This concept may be applied to various areas of engineering, e.g., artificial intelligence and neural networks in information technology are inspired by the desire to mimic human brain. The existence of biocells and deoxyribonucleic acid (DNA) serves as a source of inspiration for nanotechnologists who hope to one day build self-assembled molecular-scale devices. In the field of biomimetic materials, there is also a whole area of bioinspired ceramics based on sea shells and other biomimetic materials.

In the field of biomimetic surfaces, a number of ideas have been suggested so far [24, 25, 132, 279]. These include the lotus-leaf surface, which has superhydrophobic and self-cleaning properties; the gecko foot, which has very high and adaptive adhesion; the moth eye, which does not reflect light; shark skin, which can suppress turbulence while moving underwater while; the water strider leg, which stays dry atop a pool of water; the darkling beetle, which collects dew using hydrophilic microspots; and the sand skink, which reduces friction using nanothresholds. The common feature found among many of these surfaces is that they have hierarchical roughness with rough details ranging from nanometers to millimeters. This observation inspired us to study multiscale frictional dissipative mechanisms in combination with hierarchical surfaces.

Multiscale Dissipative Mechanisms and Hierarchical
Surfaces

Friction, Superhydrophobicity, and Biomimetics

Nosonovsky, M.; Bhushan, B.

2008, XVIII, 278 p. 112 illus., Hardcover

ISBN: 978-3-540-78424-1