

1 Introduction

Definitions and Classification

1.1 What Are Network Materials?

The word “network” is important today in many areas of science and engineering. Communication networks, including social networks, transportation systems such as the system of roads and railroads, energy transportation networks, water and sewer systems, and the circulatory system of animals, are examples of networks whose essential role is to transport matter or information. On the other hand, physical networks made from connected filaments are broadly encountered in biology and engineering and perform mechanical functions.

Many biological materials are constructed from fibers. Spanning a volume with fibers is much cheaper than filling the same volume with a continuum material. Since the living organisms of our world build with proteins, and proteinogenic amino acids are expensive to produce, building with less material is a condition for survival of the species. The solution adopted by nature to address this challenge is to build with fibers.

Materials engineering is less constrained by energetic requirements than biology. We build with space-filling materials with little or no free volume, which one may call three-dimensional materials. Structures are also built by assembling plates and membranes, which one may call two-dimensional building blocks, and/or filaments, that is, one-dimensional, fiber-like building blocks. Some of the most versatile and cheapest materials ever developed by humans are made from fibers. And, in most of these materials, the fibers are connected into a network that spans the occupied volume.

The class of Network Materials includes materials that contain a fiber network as the main structural component and in which the network controls the overall mechanical behavior.

The fact that the material contains volume not occupied by fibers is essential in defining its mechanical properties. In the presence of free volume, fibers have sufficient kinematic freedom to change orientations, group and form bundles, or reorganize in other ways, which conveys interesting properties to the ensemble. The discrete nature of the material remains important, as the building blocks and their interaction define the overall response. Collective deformation modes, including in some cases modes of zero stiffness similar in nature with the situation of mechanical mechanisms, become not only possible, but also a common occurrence in network materials. The microstructural multistability of these mechanism-like structures leads to specific mechanical behavior under large deformations.

Interactions are de-localized; they take place at distances comparable with the length of network segments and involve not only forces, but also moments. This is in sharp contrast with monatomic lattices in which interactions are short ranged and generally result from the interplay of strong attractive and repulsive forces. While crystals have high stiffness and strength and may exhibit only those deformation modes allowed by the crystal symmetry, network materials are typically soft and their anisotropy may be tuned by controlling the distribution of fiber orientations.

The open internal structure of network materials allows for the presence of a matrix. If the network is embedded in a solid continuum, the exceptional properties emerging from the collective deformation of network fibers are largely lost, while the mechanical behavior of the composite is defined by the superposition of contributions due to the matrix and individual fibers. However, if the matrix is a fluid, not only is the network behavior preserved, but the interaction between fibers and the fluidic matrix may lead to interesting effects not present in dry networks without a matrix. Also, the network may embed inclusions, entities which modify the local network behavior and lead to significant changes of the global performance. An amazing network material of this type is cartilage, which inherits its properties from the presence of embedded macromolecular entities – the glycosaminoglycans – which are not part of the underlying network.

In all biological network materials, the network structure is stochastic. Likewise, the vast majority of man-made network materials have stochastic network structures. Woven textiles are a notable, but singular exception from this rule. Stochasticity enables a diversity of local deformation modes, including collective modes. Structural stochasticity conveys material resilience and defect tolerance, leading to increased strength and toughness.

Some materials made from fibers do not exhibit the network signature and cannot be classified as network materials. Densely packed fibers held together by strong surface interactions form a continuum. An example of this type is provided by insect cuticles made from chitin fibers arranged approximately parallel to each other, strongly bonded, and tightly stacked, forming anisotropic continuum layers. For the same reason, usual fiber composites cannot be classified as network materials. In short fiber composites, fibers may not interact strongly with each other and may not form a network. In continuous fiber composites, the woven reinforcement is embedded in a stiff matrix aimed to strongly restrict the kinematic freedom of the fibers and to eliminate the signature of the network. In such composites, the goal is for the material to inherit the properties of individual fibers – primarily their high stiffness and strength. Polymeric materials are composed from chains which, if long enough, organize in a network. The signature of the network appears at temperatures above the glass transition temperature, T_g , when filaments are able to move relative to each other. Below this temperature, chain kinetics as well as network collective deformation modes are frozen. Polymers below T_g cannot be classified as network materials due to their dense packing and strong surface interactions, which limit chain mobility.

A large number of examples of network materials can be given. The following list is provided for exemplification, but it is not exhaustive. From the range of man-made engineering network materials, one may mention:

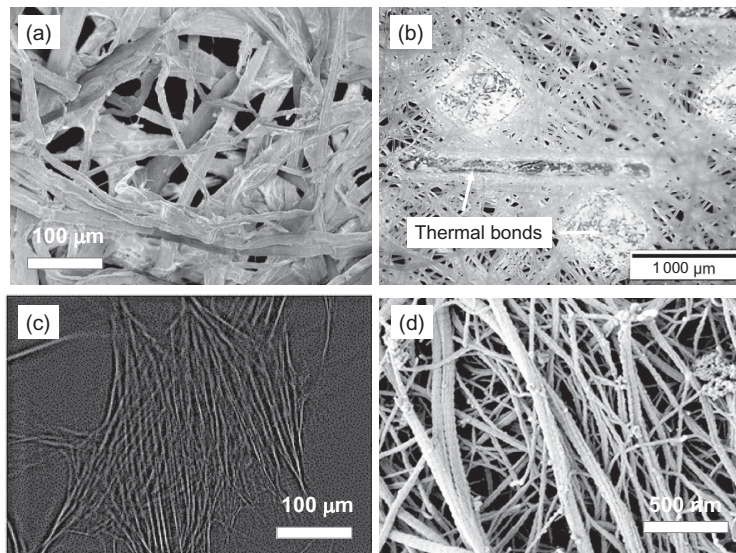


Figure 1.1 Examples of network materials: (a) absorbent, high porosity paper, (b) thermally bonded polypropylene nonwoven with rectangular and square thermal bonds, (c) stress fibers in the cytoskeleton (reproduced with permission from Alioscha-Perez et al., 2016), and (d) collagen structure of arthritic human knee cartilage. Reproduced with permission from Gottardi et al., 2016

- ▶ **Paper, Parchment, and Papyrus.** All three are network materials used as supports for writing. The oldest of these is papyrus, which was used in Egypt as far back as 2 500 BC. Papyrus is made from the stem of the *Cyperus Papyrus* plant cut longitudinally and arranged in layers with the direction of the natural fibers orthogonal to each other in subsequent layers. The stack is pressed and dried under pressure to produce a relatively rigid layered fibrous structure. Papyrus was used in Europe until about year 1 000 CE, when it was replaced with parchment. Parchment is made from animal skin processed in a strongly alkaline solution and dried under tension. The process leaves primarily the underlying collagen network of the skin known as the dermis, which is a relatively high strength and high toughness network material in hydrated conditions. Drying makes the material more brittle. Paper dates from about 2 000 years ago and was imported in the Western world from China. It is made from cellulose fibers which are pressed together in the wet state and dried under pressure. Papers with a broad range of mechanical properties are made today, ranging from very soft, low density tissue, to the higher density paper on which this book is printed, and to the resilient multilayered paper of the absorbent kitchen towels. Figure 1.1(a) shows a scanning electron micrograph of an absorbent kitchen paper towel which evidences the porosity of this material. Printing paper is made from similar ribbon-like cellulose fibers packed densely.

- ▶ Textiles, woven. Weaving is one of the oldest occupations of humans. Woven fabrics are made by interlacing two or multiple threads. The threads are made from natural fibers, such as cotton and hemp, or from polymeric fibers. The threads are continuous, while fibers are short and are twisted to form threads. The structure of fabrics is periodic, which is rather unusual for a network material. The deformation behavior of the fabric is controlled by the mechanics of the periodic unit cell and the essential inter-fiber interactions are topological. Weaving entangles the threads, which ensures that the fabric preserves integrity and sustains loads even though the threads are not crosslinked and are not held together by attractive surface interactions. Today, textile engineering is an important field that assists a vast industry. All of us use these versatile, cheap, and mechanically performant network materials throughout our entire life.
- ▶ Textiles, nonwoven. Nonwovens are a newcomer to the world of textiles. While older versions such as felt have been produced from natural fibers for a while, the modern nonwovens are made primarily from polymeric fibers, which are spun and deposited on a conveyor belt, followed by calendaring and, in most cases, by thermal bonding. The result is a stochastic mat-like network of “infinite” fibers of 10–50 μm diameter. An as-deposited nonwoven mat has low stiffness and high porosity. To increase the stiffness and strength, fibers may be entangled by exposure to water jets (hydroentangled), may be pressed under moderate heat, which causes weak bonds to form at all fiber contacts (heat sealed), or may be thermally bonded by bringing them in contact with heated punches which melt the fibers they touch. The solid polymeric blocks formed subsequently at the location of thermal bonds create effective crosslinks between fibers (Figure 1.1(b)). Nonwovens are used in many applications, such as geotextiles, packaging materials, air and water filters, structural materials for consumer products, such as wipes, tissue, and disposable diapers, scaffolds for tissue engineering, etc. Nonwovens made from nonpolymeric materials, such as fiberglass, are used for thermal and sound insulation in buildings and automobiles. And how could one not mention the most visible application of nonwovens during the time when this book was written: the surgical and N95 masks worn by everyone during the COVID-19 pandemic of 2019–2022.
- ▶ Gels. Gels are molecular networks embedded in a liquid. The network is swollen by the liquid, the molecular strands making sparse or no contacts with each other. The network is held together by crosslinks which may be strong chemical bonds (in chemical gels), helical domains (in physical gels), small crystallites, or regions of ordering in which the molecular strands are held together by weak hydrogen bonds. Transient gels form in dense suspensions of high aspect ratio flocculants, which may be macromolecular or fiber-like. Cohesive and dispersive forces acting between suspension components lead to their aggregation in a percolated network structure. Such networks are weakly bonded and may re-organize dynamically during flow. They exhibit the rheological property of thixotropy, that is, behave as solids with a yield point at small loads, but flow like fluids at loads larger than the yield stress. Gel properties cover a broad range from a very soft and brittle, to a

relatively stiff and tough, function of the nature and density of the crosslinks, the type of filaments forming the network, and the interaction between filaments and the embedding liquid. Gels are used in many applications in the food and cosmetics industries, in paints and adhesives, and in biomedical applications. In a broader sense, most network materials encountered in biology are hydrogels, in which the network is made from protein fibers and the embedding fluid is water.

- ▶ **Elastomers.** Elastomers are networks of long and flexible molecules that interact through strong covalent bonds at a small number of sites, and through weak interactions elsewhere. The strong bonds represent crosslinks which, in the majority of the elastomers, are permanent. Weak interactions hold the molecular strands together at melt densities. The resulting network has low free volume, but inter-molecular interactions at sites other than those of the crosslinks are weak and molecular strands are free to move relative to each other, allowing for network reorganization during deformation. This is a situation somewhat different from that of other network materials in which the large free volume available allows the type of fiber kinematics which ultimately defines the mechanical behavior of the network. While most elastomers are thermosets, some are thermoplastic and may be reshaped at elevated temperatures. This is possible due to the dissociation of the crosslinks at higher temperatures, which transforms the solid network into a viscous melt. The network reforms upon cooling and the elastomeric properties are recovered. Elastomers may sustain large, reversible deformations with limited internal dissipation. They are used in many applications, either as pure network materials, or filled with nanoscale inclusions such as carbon black. The filled elastomers have one of the most impressive sets of mechanical properties of all current materials; consider the extreme loading conditions to which automobile tires are subjected and the excellent lifetime of filled rubber.
- ▶ **Other polymeric networks.** Polymeric materials are made from chains packed at high densities. The chains form a load-transmitting and system-spanning network which defines the mechanical properties of the material. The condition for these systems to be classified as network materials is that the chains have sufficient relative mobility to allow network structural evolution during loading. For example, reducing the temperature below the glass transition temperature reduces the mobility of the chains and freezes topological rearrangements. Under such conditions, the macroscopic response is defined primarily by the dense nonbonded interactions, and less by the underlying network. Above the glass transition temperature, dense polymeric solutions and melts may be entangled and exhibit solid-like behavior at probing frequencies above the inverse of the disentanglement time. These materials exhibit the behavior of a Newtonian liquid at probing frequencies below this threshold.

The first three examples in this list – paper, and woven and nonwoven textiles – and the following three examples – gels, elastomers, and polymeric networks – are classified in separate categories based on the sensitivity of their response to temperature variations. The networks in the first group are denoted as *athermal*, while those in

the second group are *thermal*. As the name indicates, the behavior of the first group is largely independent of temperature, while the mechanics of networks in the second group are strongly influenced by thermal fluctuations. This distinction can be interpreted in terms of the energy required to deform individual filaments. If filaments are thin and their bending stiffness is low, thermal fluctuations have sufficient energy to perturb filament conformations. This has a strong influence on the mechanical behavior of networks composed from such filaments, which therefore can be classified as thermal.

Network materials are the structural materials of living organisms. A large number (if not the majority) of biological materials have a fiber network as their main structural component:

- ▶ The cellular cytoskeleton. All eukaryotic cells contain a filamentary network structure in which the cellular organelles are embedded. This network is composed from three types of protein filaments: actin filaments (F-actin), intermediate filaments, and microtubules. The cytoskeleton performs multiple roles: it provides the mechanical structure of the cell, it mediates connections across the cell membrane between neighboring cells, it contributes to mechano-transduction, which converts force into biochemical signals, and it supports transport to and from the nucleus. F-actin filaments are connected by actin-binding proteins and by myosin motors able to apply forces between actin strands, which renders the network active and makes cell migration possible. Under normal conditions, a cell attaches to the neighboring cells and/or to the substrate and pulls; hence the cytoskeleton is under pre-stress due to the action of myosin motors. The F-actin network is also highly transient, as filaments grow at the leading edge of cytoskeleton protrusions and degrade to the constituent monomers at retracting sites. This behavior renders the mechanics of the cytoskeleton highly complex. Due to its key role in sustaining life, the physics of the cytoskeleton is intensely studied at this time. Figure 1.1(c) shows an image of stress fibers formed by the reorganization of actin filaments under stress produced by myosin motors (Alioscha-Perez et al., 2016). The sites where the cell is attached to the substrate are visible along the periphery of the fibrous structure.
- ▶ Fibrin. Fibrinogen is a protein which exists in blood. Under the action of the enzyme thrombin, it polymerizes, forming fibrin filaments. This process is triggered by a biochemical cascade when the lining of the blood vessels is broken. Platelets in the blood agglomerate at the wound site and trigger the polymerization of fibrinogen. Fibrin filaments grow to connect and embed the platelets, forming a blood clot. This mechanism is the hemostatic first step of wound healing, but it is also central in cardiovascular disease. The fibrin network contracts as it forms due to the dynamic formation of crosslinks and cohesive interactions between filaments. This mechanism densifies the clot and ensures its mechanical integrity and stability.
- ▶ Collagen networks. Collagen is the most abundant protein in the human and animal bodies. It forms fibers composed from tropocollagen triple molecular

strands. Networks of collagen fibers are present everywhere in the body, providing structural and mechanical functions. The collagen network denoted generically as an extracellular matrix provides mechanical and biochemical support to the cells. The mechanical function of membranes and connective tissues is also performed by collagen networks. Cartilage, tendons, and ligaments are collagen networks with specific architecture adapted to the function of the respective tissue. The dermis, the basement membranes, the amnion, and the liver capsule have collagen networks as their main structural component. The elasticity of blood vessels is provided by networks of collagen and elastin. Collagen exists in bones and regulates the bone toughness. It is difficult to overestimate the importance of this type of fiber network in biology. Figure 1.1(d) shows a scanning electron micrograph of cartilage from an arthritic human knee, after enzymatic depletion of proteoglycans and chondrocytes (Gottardi et al., 2016). The image shows thicker bundles, of approximately 200 nm diameter, along with thinner fibers. The presence of the thinner collagen fibers is a result of the degenerative disease.

The first two examples in this list – actin and fibrin – are thermal networks, while the third example – collagen – is of athermal nature. Collagen is a protein fiber composed from molecular strands of tropocollagen which, just like actin, fibrin, and other bio-filaments, are small enough for their mechanics to be affected by thermal fluctuations. However, tropocollagen assembles in larger fibrils, which then bundle to create the collagen fiber bundles that become the building blocks of the extracellular matrix. These collagen bundles are sufficiently large to be athermal (Figure 1.1(d)). Further, it should be noted that most bio-filaments, including actin, are relatively stiff in bending and have large persistence length. In order to differentiate them from flexible polymeric chains with small persistence length, these filaments are called semiflexible. The distinction between flexible and semiflexible filaments is made only in the context of thermal networks and implies a comparison of two length scales: the filament persistence length and the mesh size of the network. If the persistence length is larger or comparable with the mesh size, the semiflexible nature of the filaments has a signature in the overall mechanical behavior of the network. If the mesh size is much larger than the filament persistence length, the mechanical behavior is similar to that of a network of flexible filaments.

1.2 Classification

Network materials may be classified based on various criteria. Three criteria are used here to divide networks into several broad categories that emphasize important commonalities between some apparently very different material systems.

The three criteria used are: (i) the presence in the material of components other than fibers, (ii) the nature of the interactions that stabilize the network, and (iii) the type of fibers forming the network.

Table 1.1 shows the classification in terms of criterion (i). Network materials are divided into three categories: networks composed exclusively from fibers, which are

Table 1.1 Classification of network materials based on the presence of components other than fibers

| Dry | Embedded | Embedding |
|-----------------|-----------------------------|--|
| Paper | Gels | Cytoskeleton |
| Nanopapers | Entangled polymer solutions | Connective tissue |
| Textiles–woven | Connective tissue | Extracellular matrix |
| Nonwovens | Dense fiber suspensions | Fibrin |
| Elastomers | | Composites in which a dry networks performs the function of matrix |
| Thermoplastics | | |
| Thermosets | | |
| Fiberglass/Felt | | |
| Open cell foams | | |
| Mycelium | | |

Table 1.2 Classification of network materials based on the interactions that stabilize the network

| Crosslinked | Entangled | With Surface Interactions |
|----------------------|----------------------------|----------------------------|
| Paper | Textiles–woven | Buckypaper |
| Nonwovens | Nonwovens | Nanopapers |
| Elastomers | Fiberglass/felt | Fibrin |
| Thermosets | Thermoplastics above T_g | Thermoplastics above T_g |
| Gels | Dense fiber suspensions | Dense fiber suspensions |
| Connective tissue | Elastomers | Elastomers |
| Extracellular matrix | | |
| Fibrin | | |
| Open cell foams | | |
| Mycelium | | |
| Cytoskeleton | | |

denoted as “dry” networks, networks embedded in a continuous matrix, which may be solid or liquid, and networks that embed inclusions, indicated in Table 1.1 as “embedding.” Many of the man-made network materials are used in the dry state. All biological network materials are of embedded and/or embedding type. From the mechanical behavior perspective, each of these classes poses specific problems. We take the view that the fundamental network behavior is that of dry networks, while the presence of a matrix and/or inclusions leads to modifications of this basic response in ways dependent on the nature of the added phases. The mechanical response of each of these three types of networks materials is discussed in separate sections of the book.

Table 1.2 shows the classification in terms of criterion (ii): the nature of interactions that stabilize the network. One may distinguish three categories: networks stabilized by crosslinking, networks stabilized by topological interactions between tortuous fibers, and networks stabilized by surface interactions such as cohesion. In most cases, multiple types of interactions operate concurrently and stabilize the network. For example, the mechanical behavior of nonwovens may be controlled by both crosslinks

Table 1.3 Classification of network materials in terms of the types of fibers forming the network

| Athermal | Thermal | |
|----------------------|----------------------------|------------------------|
| | Flexible | Semiflexible |
| Paper | Elastomers | Cytoskeleton |
| Textiles–woven | Thermoplastics above T_g | Fibrin |
| Nonwovens | Gels | Other protein networks |
| Fiberglass/Felt | | |
| Open cell foams | | |
| Mycelium | | |
| Connective tissue | | |
| Extracellular matrix | | |
| Buckypaper | | |

and inter-fiber contacts/entanglements (excluded volume interactions), while one of these may dominate in a specific range of network and crosslink densities. Likewise, in the extracellular collagen matrix, bundle crosslinking is essential, but bundles are stabilized by strong surface interactions between fibrils.

Table 1.3 presents the classification based on the third criterion, which takes into account the nature of the fibers composing the network. We differentiate between athermal and thermal networks. Biological and artificial network materials can be classified either as thermal or athermal, depending on the dimensions and bending rigidity of their filaments. Thermal networks are classified further as being composed from flexible and semiflexible filaments. Molecular networks in which the molecules do not bundle are generally thermal. Networks made from fibers of filament bundles of diameter larger than a few hundred nanometers are generally athermal.

A note on the terminology used is necessary at this point. Here and throughout this book the terms “fiber” and “filament” are used somewhat interchangeably. “Filament” is used to denote fibers of small, submicron cross-sectional dimensions, both thermal and athermal. The term “fibers” is used generically but implies athermal behavior. Molecules are referred to either as “strands,” “chains,” or “filaments.”

1.3 Outline of the Book

The objective of this book is to define and establish the class of Network Materials and to review the common features of their mechanical behavior. The focus is on stochastic structures, because these are widespread in nature and in engineering applications, and on mechanical behavior, because the main function of the underlying network is structural. We exclude textiles and continuous fiber composites which have periodic structure and discuss only certain aspects of entangled polymeric solutions and melts; the topics not discussed in detail here are addressed in dedicated texts.

The book is organized into 11 chapters which develop the subject starting from the building blocks of network materials to the complexities of the mechanical behavior of time-dependent and composite networks.

Chapter 2 provides an overview of the mechanical behavior of the three main types of fibers: athermal, thermal flexible, and thermal semiflexible. The linear, nonlinear, and rupture aspects of the behavior are discussed. Since in many practical situations networks are composed from bundles, elements of the mechanics of fiber bundles are presented in the second part of Chapter 2.

Chapter 3 discusses the interactions taking place between fibers. Fibers come into contact either in a crossed geometry or all along their length. Crosslinks or simple contacts with purely repulsive or with cohesive interactions are established in the crossed case. Contacts characterized by a specific work of separation are established when fiber axes are parallel. The mechanics of crosslinks and the separation and relative sliding of various types of contacts are discussed in detail.

Network materials have stochastic structure. Since the number of configurations of fibrous assemblies is infinite, it is necessary to inquire about the minimum set of parameters needed to describe the aspects of the structure most relevant for the mechanical behavior of the network. This is the subject of Chapter 4. Thermal and athermal networks, cellular and fibrous networks with and without fiber tortuosity, defined in two and three dimensions are considered. The porosity of the network – a parameter important both in fluid transport across networks and in mechanics – is analyzed and is placed in relation with other structural parameters.

The deformation of stochastic networks is nonaffine, meaning that local strains are different from the global applied strains and vary spatially. However, assuming that the deformation is affine allows us to derive analytic constitutive descriptions which cannot be obtained in the general, nonaffine case. The affine description may be taken as a reference for the more accurate characterization that accounts for nonaffinity. The affine description is also of historical importance. Due to these reasons, a separate chapter is dedicated to this model (Chapter 5).

Chapter 6 presents the key aspects of the mechanical behavior of thermal and athermal network materials. The chapter is divided into two parts, referring to cross-linked and non-crosslinked networks. The section addressing crosslinked networks discusses uniaxial tension, uniaxial compression, and multiaxial loading situations separately. For each type of loading the generic aspects are presented first, as they emerge from computer models and experiments. The relation between various aspects of the behavior and network parameters is analyzed in detail. The effects of connectivity, fiber alignment, fiber tortuosity, crosslink compliance, and elastic–plastic behavior of the fiber material are discussed. This establishes the structure–properties relations needed in material design. The behavior described is demonstrated using representative experimental data for a variety of network materials. Size effects, that is, the dependence of the mechanical response on the sample size, are also discussed. The section on non-crosslinked networks has two parts outlining the response of athermal non-crosslinked fiber masses to compression, and the role of topological interactions (entanglements) in defining the response in tension.

Chapter 7 presents a review of constitutive descriptions developed for network materials, with emphasis on micromechanics. Constitutive models are required by continuum representations of fibrous materials, but the complex behavior emerging from the collective kinematics of the fibers is generally difficult to capture by mean field representations. The chapter presents a review of the state of the art in this area.

Chapter 8 focuses on the strength of network materials. It has two parts, referring to athermal and thermal networks. Each of these presents two topics: Strength in the absence of pre-existing cracks or damage; and the growth of a pre-existing flaw. The failure modes and mechanisms, the relation between strength and network parameters, the effect of fiber alignment, fiber tortuosity, variability of fiber properties, and the size effect on strength are analyzed. In the context of thermal networks, a summary of key results from the vast literature on rubber failure under monotonic and fatigue loading conditions is presented. Since network materials are occasionally used as adhesives or as a matrix for composites, it is important to explore the design paths that may lead to increased toughness without loss of strength. A section of Chapter 8 is dedicated to the development of tough network materials.

The mechanical behavior of some network materials is time dependent. Network-scale time dependence emerges from a variety of sources, including the fact that the fiber material behavior may be rate-sensitive, the presence of dissipative interactions between fibers, viscous friction at contacts between athermal fibers, the flow of solvent in and out of the network, and the presence of transient crosslinks. These mechanisms, their interaction, and influence on the mechanical behavior of the network are discussed in Chapter 9.

Chapter 10 presents the effect of surface interactions on the mechanical behavior of networks. Surface interactions are important in non-crosslinked networks of flexible filaments. Two types of systems are considered: dense suspensions of filaments that self-organize, forming percolated and transient network structures, and dry networks self-organized by cohesive forces. In suspensions, the fluid develops solid-like behavior manifest at relatively small strains due to the presence of the self-organized network structure. Surface interactions produce fiber bundling and networks formed exclusively from fiber bundles emerge. Networks of fiber bundles are fundamentally different from both the crosslinked and non-crosslinked networks discussed in Chapter 6.

Chapter 11 presents an analysis of composite networks. This class includes network materials reinforced with spheroidal inclusions or with staple fibers much stiffer than the base network fibers. Interpenetrating networks formed by two or multiple cross-linked networks which span the same problem domain are also composite networks and are discussed in this chapter. A crosslinked stochastic network embedded in a solid continuum matrix is a special type of composite, which is marginally related to the usual fiber composites. A section of Chapter 11 is dedicated to this topic.

A number of emerging topics are left out from this book. These include sub-isostatic networks, networks with pre-stress, active networks, tensegrity structures, and the developing sub-field of metamaterials. In sub-isostatic networks the condition of stability of the structure is not fulfilled in the unloaded state. These networks are

mechanisms and have zero stiffness when probed at small strains but acquire stiffness upon further straining. Their mechanical behavior is more sensitive to the details of the network architecture than that of a stable isostatic network because such structures function in the proximity of a critical point, that is, the state in which they shift from being sub-isostatic to isostatic.

Pre-stress modifies the mechanical behavior significantly, as expected in a non-linear system. Specifically, pre-stress stiffens the network, renders stable isostatic networks below the stability limit, and decreases the strength of networks. The use of pre-stress to systematically modify network behavior was not explored extensively to date in the context of applications.

The cytoskeleton is an active network material of obvious importance. Many aspects associated with activity in this complex network have been studied, while others await systematic examination. The design of active engineered networks has been discussed in the literature, particularly in the context of periodic network structures. However, this sub-field is emerging and its impact is uncertain at this time.

Metamaterials are generally periodic fiber-based structures whose architecture is designed such as to provide a pre-defined material-scale behavior. The network may undergo internal instabilities both on the repeat unit scale, as well as on the global scale. Since this book focuses on stochastic networks prevalent in the biological world and in contemporary engineering applications, metamaterials are not discussed. However, many results presented in Chapter 6 also apply to this class of structures. Further details are available in recently published texts on metamaterials (e.g., Lakes, 2020).

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