Modeling the Structural Development and the Mechanics of Complex Soft Materials: Overview

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Contents

Abstract

The materials discussed in the chapters of this section are apparently very different from each other (ranging from soft gels to cement and clays), but they all share structural and dynamical complexity that cover a range of length scales. Distinct computational approaches are required for the different length scales or timescales, and a statistical analysis of spatiotemporal fluctuations is crucial

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to develop a deeper fundamental understanding of the material properties. Here we provide an overview of the different chapters, to highlight the connections between them and outline the emerging scientific questions.

1 Introduction

Most of the materials of interest in our everyday life and in the technological world have structural and dynamical complexity that extends over a wide range of length scales and has enormous impact on the material behavior (response to environmental changes, evolution over time etc.), posing formidable challenges to rationalizing and predicting it. Modeling and computational approaches need to address such complexity, in order to provide meaningful answers and insight. Soft materials like gels are an example and have emerged as pivotal in technologies ranging from food to personal care, smart electronics, or biotechnologies, because they can be easily processed (they can be easily stretched, squeezed, or made to flow, Fig. 1) and they have tunable mechanical properties (▸ Chap. 70, "Mechanics of Soft Gels: Linear and Nonlinear Response"). Materials such as cements or clays are not usually regarded as soft since they are mainly used in their hardened state, but it is when they are soft, while solidifying or setting, that their final microstructure develops and their distinctive properties emerge (▸ Chaps. 71, "Mesoscale Structure and Mechanics of C-S-H"; ▸ 72, "Nanoscale Composition-Texture-Property-Relation in Calcium-Silicate-Hydrates"; ▸ 73, "From Microscopic Insight to Constitutive Models: Bridging Length Scales in Soft and Hard Materials"). In all cases, disentangling structure development, dynamics, and mechanics over different length scales is needed to achieve an adequate understanding of the material properties and hence to be able to predict them.

The chapters in this section revolve around this theme: how can modeling and computational approaches include enough details of the chemistry and of the microscopic structure to capture the essential and distinctive features of such complex materials? What is the appropriate level of details needed? In which conditions can more abstract and coarse-grained or mesoscale models provide useful

Fig. 1 Complex materials, soft and hard. This section covers modeling and computational approaches for materials soft as food and hard as concrete. Crucial for all those materials is to be able to capture the development of the microstructure when they solidify. As in glasses, the resulting microstructure lacks long-range order and features frozen-in stresses that have impact on the mechanics

insight and how? How can the insight and understanding gained through modeling and computational studies contribute to the technological and societal concerns that these materials carry?

2 Microstructural and Dynamical Complexity: From Food to Cement

Gels typically comprise a soft, porous and prevalently elastic matrix or solid network interspersed in a fluid (which can be a simple Newtonian liquid or a more complex viscoelastic medium). In many cases, the porous matrix is self-assembled from colloidal or larger units that can also be aggregates, fibers, or bundles hierarchically organized. The units that compose the large-scale structure of these materials are, therefore, already complex to start with (e.g., in most gels of interest for food the colloidal units are proteins), and the additional level of organization into larger-scale structures can add further layers of complexity. Modeling and computational approaches that start from an atomistic description of these materials are typically limited to a very narrow range of length scales that are far from covering the structural, dynamical, and mechanical properties emerging from the larger-scale structure and used in the engineering applications. Coarse-grained models and numerical approaches that do not provide an atomistic description but are able to capture the essential ingredients of the self-assembled, larger-scale structure (e.g., size distributions of pores, aggregates, etc.) are therefore extremely important to unravel the relationship between microstructural features and material behaviors (▸ Chaps. 70, "Mechanics of Soft Gels: Linear and Nonlinear Response"; ▸ 71, "Mesoscale Structure and Mechanics of C-S-H"; ▸ 73, "From Microscopic Insight to Constitutive Models: Bridging Length Scales in Soft and Hard Materials"). All materials of interest are structurally amorphous solids, and their microstructures correspond to non-equilibrium, metastable states that have frozen-in stresses that depend on the material history. As a consequence, the way the microstructure develops has a significant impact on the material properties and hence has to be properly incorporated in the modeling. The chapters in this section give several insightful examples of how the structural disorder, the complexity in terms of length scales covered, and the history dependent nature of the microstructure, can be taken into account.

Concrete and cement do not come to our mind when discussing *soft* gels. Nevertheless, they are relatively close to soft gels, while cement is setting and its nanoscale amorphous structure is further developing and densifying (▸ Chap. 71, "Mesoscale Structure and Mechanics of C-S-H"). In fact, as cement dissolves in water the dissolution of the calcium silicates contained in the powder produces, among other hydration products, calcium-silicate-hydrates (C–S–H), the material at the origin of cement cohesion and concrete strength. During cement hydration, nanoscale C–S–H clusters (or particles) aggregate into gels that constitute the basis of the hardened cement paste used for constructions. The C–S–H gels are extremely cohesive and constitute the main binding agent in concrete, therefore crucial

to the material mechanical performances. Although various other compounds are present in concrete, the C–S–H are already chemically complex, since they exist with a range of different stoichiometries and are amorphous (▸ Chap. 72, "Nanoscale Composition-Texture-Property-Relation in Calcium-Silicate-Hydrates"). Their microstructure and properties result from a complex and strongly non-equilibrium aggregation process. Two of the chapters in this section cover the most recent advances in modeling and computational approaches for cement hydrates. In particular they represent a good example of how concepts developed for other materials, such as high-performance glasses or colloidal gels, have helped scientists develop novel fundamental understanding and insights into cement and concrete.

A common feature in the materials discussed in the next chapters is certainly the presence of frozen-in stresses, which develop as the material solidifies (▸ Chap. 73, "From Microscopic Insight to Constitutive Models: Bridging Length Scales in Soft and Hard Materials"). The internal stresses that develop during cement hydration and setting can have manifestations as extreme as swelling and shrinkage of the incipient solid and even lead to cracking. They are known to have an impact on the durability of the final product. In softer gels, the presence of frozen-in, localized stresses can be more subtle, but it is clearly revealed by the progressive aging of their mechanical properties as well as by the strain localization that characterize their mechanical response even at small deformations, in the linear response regime. Understanding how frozen-in stresses develop during solidification of amorphous materials and how they interplay with an imposed deformation to determine the mechanical response is one of the outstanding challenges in material science and technologies. Think, for example, 3D printing technologies, where one needs to finely control the final properties of the printed layers as the material is being squeezed out of a nozzle (e.g., as in direct writing), flows, and re-solidifies (Chandrasekaran et al. 2018). Controlling and suitably designing the rheological response of the ink (from soft gels to cement) is essential. To do so, a deeper understanding of the basic mechanisms that regulate the emergence and the evolution over time of the frozen-in stresses is needed. The chapters in this section analyze the problem of stress localization in amorphous structures at different levels: for example, through the atomistic disorder in C–S–H nanoparticles and through the mesoscale texture of C–S–H gels in ▸ Chaps. 71, "Mesoscale Structure and Mechanics of C-S-H," and in ▸ 72, "Nanoscale Composition-Texture-Property-Relation in Calcium-Silicate-Hydrates," or through the spatiotemporal statistical analysis of density and stress fluctuations in aging soft gels in ▸ Chap. 70, Mechanics of Soft Gels: Linear and Nonlinear Response". Different levels of description of the material at play require different methodologies, and you will find in this section a discussion of relevant techniques and strategies that could be applied to a variety of different materials. The area of computational mechanics and rheology for this type of complex materials is still nascent, but it has a great potential to connect the microstructural description of the material (even if simplified or coarse-grained) to its rheological response in a way that is still mainly inaccessible through experiments. In particular, the possibility to describe *local* stresses and strains in

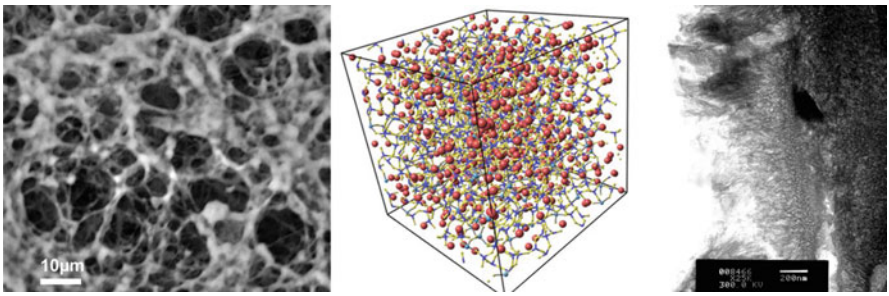

Fig. 2 Microstructural complexity in soft and hard materials. Casein gels are the basis of yogurt products: on the left a SEM image on the left a SEM image of acidified casein gel, prepared as in (Leocmach et al. 2014), courtesy of T. Divoux. Atomistic simulations highlight the structural complexity of high-performance glasses (center) (Bauchy et al. 2017). On the right, a TEM image of the nanoscale structure of cement hydrates. (Reprinted from Del Gado et al. 2014)

response to different types of deformation and deformation rates can radically deepen the current understanding of the mechanics of soft complex materials and in particular of their nonlinear behavior, as discussed in ▶ Chap. 70, "Mechanics of Soft Gels: Linear and Nonlinear Response". While these aspects are here mainly analyzed for soft gels, the next step ahead is to transfer the new concepts and insights gained across materials and technologies (Fig. 2).

Constructing methods and strategies to bring the microscopic information (e.g., chemical composition, atomistic description etc.) into coarse-grained models and, from there, into the continuum level description of the materials is an open, outstanding question. You will see it appear through in all the chapters of this section and discussed more thoroughly in ▶ Chap. 73, "From Microscopic Insight to Constitutive Models: Bridging Length Scales in Soft and Hard Materials," where we sketch a possible strategy. The modeling and computational difficulties to be faced are many and vary depending on the specific material and on the specific engineering context. An important point is that, when materials have the multiscale complexity described in the examples you will see in this section, one needs to develop different approaches at different length scales, and therefore the main question becomes how to connect those approaches.

3 Conclusions

To summarize, the chapters of this section provide examples of how modeling and computational studies can indeed address the structural, dynamical, and mechanical complexity of technologically relevant real materials. They highlight the common traits of non-equilibrium conditions, structural disorder, and frozen-in stresses in a wide range of materials from soft gels to hard cement and unravel fundamental physical mechanisms (microscopic strain and stress localization, stress relaxation, etc.) that ultimately are at the origin of behaviors such as aging, creep, failure, or yielding. The workshop on "Physics of Dense Suspensions" held at the Kavli

Institute of Theoretical Physics of UCSB in 2018 hosted a number of events and several discussions focused on the very same issues. The progress made when addressing such issues is beyond the understanding of a complex material or of a complicated behavior, because the fundamental insights gained can be immediately fed into engineering questions with practical relevance. In the case of cement, the fundamental understanding of the physical chemistry and mechanics is required for new, greener technologies to develop and emerge. Given the volume of construction industry, the role that cement and concrete play in it and the overall environmental impact of cement production for concrete, new strategies to make the material and its production smarter and more sustainable are urgently needed.

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