CHAPTER 4

EMERGENCE OF COLLECTIVE PHENOMENA: STRONGLY CORRELATED MULTIPARTICLE SYSTEMS

The Grand Challenge for Collective Phenomena is to discover how remarkable properties of matter emerge from complex correlations of the atomic or electronic constituents and to control these properties.

Crystalline diamond is both a precious gemstone and an interesting material with outstanding hardness, excellent heat conductivity, and other remarkable properties. It is also one of the simplest solids known, built from carbon atoms alone. Viewed at the atomic scale, these atoms in their equilibrium state form an intricate lattice with each carbon atom bonded to four equidistant neighbors (Figure 4.1), forming a tetrahedron, one of the five ideal solids envisioned by Plato. The bonds that tie neighboring atoms together in diamond are among the strongest in nature. Because of them, each atom influences and is influenced by its neighbors: we say that they are correlated. The net result of these atomic correlations is the existence of the crystal and its remarkable properties. For example, the hardness of diamond results from both the strength of individual bonds and the perfection of the correlations, or alternatively, the rarity of defects in the crystal. In a one-carat (0.2-g) diamond without defects, one can follow a chain of 10 million of these minute tetrahedra from one side of the crystal to the other with such precision that the relative locations of carbon atoms at either end of this chain remain fixed to within a fraction of the size of a single atom.

Such “emergent” phenomena, in which the correlated behavior of many particles (in this example, atoms) leads to an unexpected collective outcome (a crystal), are of great significance across the sciences and engineering. In the basic energy sciences that are the subject of this report, the particles may be microscopic like electrons, atoms, or molecules, or may be larger entities such as sand grains, cells in an organism, or rocks in the earth’s crust.

The concept of emergence is rather general and permeates all fields of scientific endeavor. One can readily find emergence in many examples throughout this report, including climate change, earthquakes, cell colonies, neurobiology, plasma physics, and life itself. In neurobiology for example, each neuron is a single relatively well-understood cell. Yet billions of these neurons produce consciousness. How and why?

FIGURE 4.1. Left: The diamond lattice. Each carbon atom (yellow sphere) is bonded to four neighbors in a tetrahedral arrangement. The correlations in the atomic positions in the lattice persist over macroscopic length scales. Right: An artificial gem-quality diamond made by deposition of carbon vapor. Many of the extraordinary macroscopic properties of this diamond, such as its clarity and hardness, result from the perfect correlations of the atoms in the lattice.
addressing such questions, scientists endeavor to find general answers that apply to broad classes of materials, organisms, or phenomena. For instance, the theory of symmetry breaking at phase transitions describes aspects of the solidification of crystals, of the onset of magnetism and superconductivity, and even the formation of the early universe. Uncovering the fundamental rules of correlations and emergence is the first part of the Grand Challenge of this chapter. These fundamental rules are also connected to the concepts of coherent control (Chapter 2), of the fundamental composition of matter (Chapter 3), of nanoscale communications (Chapter 5), and of matter far from equilibrium (Chapter 6).

The second part of the Grand Challenge is to achieve control over those correlations, a prospect that can only now be reasonably contemplated with the advent of tools to probe and affect particles and their correlations on the nanoscale (see Chapter 7). By understanding and controlling correlations, we can put emergence to work for us. The potential applications are as rich as the variety of emergent phenomena. Given this, we cannot hope to be encyclopedic. Our aim is instead to inform the reader of the importance of this type of scientific research, identify some of the other Grand Challenges to which it is connected, and discuss what is needed to make progress in this vital area.

CORRELATIONS AND EMERGENCE: AN OVERVIEW

A fundamental type of emergence involves correlations between electrons in crystalline materials, which induce a staggering variety of novel phenomena. Research on such materials occupies a large fraction of the physics, materials, and chemistry communities and will be the major focus of this chapter. Electrons are responsible for nearly all electrical and magnetic properties of solids. For instance, magnetism, which arises in part from the intrinsic spin of an individual electron (which can be visualized as a tiny bar magnet), only occurs through strong electron correlations, which align the spin axes of different electrons relative to one another. Magnetism in solids takes diverse forms. In ferromagnetism, known to the ancient Greeks, the spins are all parallel, and a macroscopic magnetic moment with the familiar properties of an ordinary bar magnet results. Beginning in the 20th century, an ever-increasing variety of more complex types of magnetism have been discovered, often denoted inappropriately by the single category of antiferromagnetism. These have diverse applications, such as in non-volatile information storage and reading in information technologies.

Another famous example of electronic emergence is superconductivity, in which the electrical resistance of a material vanishes, accompanied by a variety of bizarre macroscopic manifestations of quantum mechanics. Many more types of electronic correlations are under active study. Each distinct phenomenon of this type could provide new functionality for future technologies. For instance, multiferroic materials, which combine ferroelectricity (the emergence of a permanent electric polarization) and magnetism, could enable devices that couple electric and magnetic action (see Figure 4.2).

To realize the potential of such correlated-electron materials, we must control these correlations. Inspiration for the level of control that might be achieved comes from present-day semiconductors, which underlie the phenomenal success of modern electronics. Conventional semiconductors, and their successors that are only dreams today, will continue to advance our technologies and our society, from how we process information and communicate, to harvesting solar energy with efficient photovoltaic solar cells and lighting our homes and workplaces. Under ordinary conditions, however, semiconductors are weakly correlated electron materials, and this characteristic limits their functionality in key ways. A major challenge is to achieve precise processing and control for intrinsically strongly correlated materials—where these correlations are pervasive, even under ordinary conditions—similar to what is routinely achieved for semiconductors today; this flexibility together with the wealth of emergent phenomena of strongly correlated materials would open up remarkable possibilities. Correlated materials could be greatly superior to conventional materials for problems ranging from efficient charge injection in photovoltaic devices to lossless electrical transmission over superconducting lines.
Moving up the scale of lengths from electrons, we encounter correlations of atoms or molecules. The example of diamond discussed above is just one of a cornucopia of beautiful crystals that are formed by atomic correlations. Production of high-quality crystals is critical to the study of the electronic correlations just described, and has much broader applications through the optical, mechanical, or thermal properties of these materials. Synthesis of high-quality single crystals and thin films of highly correlated materials has lagged dramatically in the United States and will require renewed investments particularly with the vast reduction of research activities in industry (see Sidebar “Crystal-Growth Facilities”). Other types of atomic and molecular correlations are subtler than crystallinity and can lead to important materials such as amorphous (meaning non-crystalline) solids and glasses. These correlations, which determine the limits of the mechanical strength of such materials, are just beginning to be understood (see Figure 4.3 and Chapter 3). In soft materials, larger constituents can include polymer chains or lipid molecules that self-organize into gels, membranes, or meso-phases. Such self-organization could be used for advanced lithography of patterns that would be laborious or impossible to produce in any traditional way.

Perhaps the ultimate examples of correlations and emergence are the massively interacting networks of structures in biology that give rise to the amazing capabilities of living things. “Particles” from DNA to proteins to cells to entire organisms within an ecosystem produce large-scale behavior in ways that are largely mysterious to us. However, more detailed knowledge of these constituents and their interactions is available to scientists now than ever before, through the tools of modern biology and nanoscience (Chapter 5). Understanding and controlling correlations in biology based on recent advances in understanding of the fundamental constituents is thus another feasible but extremely difficult scientific challenge.

In the next section of this chapter, we discuss some of the remarkable science of correlated materials, as well as the prospects for, and science of, “semiconductor-style” structures built from them, which are only

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**FIGURE 4.2.** Two-stage electrical control of magnetism using multiferroics. (a) Piezoforce microscopy image reveals the ability to control ferroelectricity with an electric field in the model multiferroic BiFeO$_3$, which in turn changes the antiferromagnetic structure. (b) Photoemission electron microscopy image showing that the exchange coupling between a ferromagnet (CoFe) and the antiferromagnetism of the multiferroic controls the magnetic structure in the ferromagnetic layer. (c) A schematic that illustrates the nanoscale coupling between the multiferroic and the ferromagnet. Such a multiferroic-based device could provide an efficient link between conventional electronic logic and spin-based logic (see Sidebar “Entanglement in Chapter 2), which offers the potential for significantly reduced energy consumption compared to present-day integrated circuits.

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**FIGURE 4.3.** Images of the stress field (brightness indicates higher stress) in an amorphous “solid” mixture of two sizes of photoelastic polymer disks confined in a single two-dimensional layer. Note the intricate patterns of stress due to the complex spontaneous distribution of contacts, which becomes more filamentary as the mixture approaches the “unjammed” state (right) and the mixture “melts.” A theory of these stress correlations, necessary for predictive power, is in its infancy (see also Figure 6.5).
CRYSTAL-GROWTH FACILITIES

Functional Crystals Range in Size from 100 Nanometers All the Way up to 1 Meter, and the Facilities for their Growth Are Also Diverse in Size

Crystalline materials are at the heart of most electronic, optical, and sensing technologies and are also essential for understanding fundamental principles of condensed matter. The size scale at which a material becomes “crystalline” depends on its use. Polycrystalline materials, synthesized to determine the basic electronic or magnetic response, are composed of grains of single crystals typically 100 nm in size. Large single crystals, such as those used for optical frequency conversion for the large lasers at the National Ignition Facility (Lawrence Livermore National Laboratory) are roughly 1 m in size.

Not surprisingly, facilities for crystal growth also span a range of sizes. Some crystalline materials form from the melt, much like sugar crystals grown from a solution of water. When the solutions melt at low temperature and are non-toxic, like water, an inexpensive box furnace will suffice for high-quality crystal growth. However, many compounds of interest dissolve only at very high temperatures (greater than 1500 C) or in toxic fluxes (e.g., lead, bismuth, and hydrochloric acid) and require greater infrastructure investments for safe operation. Certain compounds, usually involving volatile elements, must be grown at high pressure (many kilobars). Finally, other elements require combinations of such growth conditions, thus adding to the complexity of infrastructure.

When crystals are synthesized for industrial applications, such as semiconductor devices or optical components, cost considerations drive the development of large single-crystal boules. Modern apparatuses (see Figure 1) are required not just for the manufacture, but also for R&D of such materials.

Even for fundamental science, requirements for large crystal size (e.g., for neutron scattering) or extremely high purity (e.g., for novel semiconductor compounds) have driven the development of crystal-growth apparatuses that fall

**FIGURE 1.** Float-zone furnaces are used for the growth of large high-purity crystals. **Left:** Pressure floating-zone apparatus. **Right:** Examples of crystals grown in this way: a classic strongly correlated system—a heavy fermion superconductor (UR1.9 Re0.1 Si2) lightly doped with rhenium—and silicon.
into the mid-scale instrumentation category. A prime example is the optical float-zone furnace, which has become the workhorse for growth of large high-purity crystals of oxide compounds. In such an apparatus, the use of optical energy to create a molten zone obviates the crucible, thus releasing limitations on crystal size and purity. Such oxide crystals are required for scanning-probe microscopy, neutron scattering, and angle-resolved photoemission of strongly correlated phenomena that challenge the present understanding of matter.

It is important to emphasize the interplay of different crystal-growth techniques in the maturation of an important material. This can be illustrated no better than in the case of high-temperature superconducting copper oxides. The basic phenomenon of superconductivity in this class of materials was discovered in polycrystalline samples grown in simple furnaces. The phenomenon of high-$T_c$ is so exotic and challenging, however, that high-purity crystals, such as those grown in optical float zone furnaces, are required to understand the fundamental mechanisms at play. This example, as well as many other recent examples, shows that to fully promote the discovery and understanding of new compounds for either science or technology, crystal-growth facilities with a wide range of infrastructure size and capability will have continued relevance.

beginning to be achieved in the laboratory. Following this, we turn to examples of strong correlations in other areas of basic energy sciences, and then discuss what is needed for progress in this Grand Challenge area.

CORRELATED ELECTRON MATERIALS AND HETEROSTRUCTURES

Semiconductors enable the most influential technologies of our time, and semiconductor devices pervade every aspect of life. The spread of cell phones and the Internet throughout society is changing the fundamental nature of human interactions. Within pure science, the impact has been similarly dramatic, with at least four Nobel prizes attributable directly to semiconductor materials, including the 1956 prize for the discovery of the transistor in silicon and the 1998 prize for the fundamental physics of the fractional quantum Hall effect in gallium arsenide. These two discoveries were both enabled by advances in the creation and understanding of heterostructures (structures combining different materials). The trillion-dollar global semiconductor industry that arose from the phenomenal success of the transistor now also promises to address energy and global warming challenges through more cost-effective and efficient photovoltaic cells and lighting.

Several factors have contributed to the dramatic success of semiconductors. From a materials point of view, they can be consistently produced with very high quality and fabricated via scalable, high-throughput manufacturing into complex structures. Their key scientific properties are their sensitivity to small perturbations, such as chemical doping and applied electric fields, and the simplicity with which this sensitivity may be described. Semiconductor research is a thriving and important part of the study of hard materials with numerous impacts in basic energy sciences.

Despite all their advantages, there are limitations to current semiconductor materials and devices, and there is no doubt that tantalizing new capabilities might be possible with a departure from this paradigm. Semiconductors are materials with intrinsically weakly correlated electrons: the electrons in the semiconductor act approximately independently of one another. This is a reason for their simplicity, but it is also a limitation. Much richer phenomena can occur in materials in which particles are highly interdependent. In fact, correlation physics is observed in semiconductors under extreme conditions of ultra-high purity, very low electron density, very low temperature, and especially very high magnetic fields. Away from such extremes, however, we suggest that a promising direction for new science and technology that goes beyond conventional semiconductors is to utilize materials that naturally incorporate strong correlations.

Specifically, we envision a major effort to reproduce the amazing progress of semiconductor physics, chemistry, and materials science in new correlated-electron materials, which could create entirely new functionalities as well as higher information densities and processing
speeds than possible today with conventional materials and approaches. The resources and facilities needed for the success of this effort are discussed at the end of this chapter and in Chapter 7.

What Led to the Success of Semiconductors?

The combination of factors that led to the remarkable success of semiconductors is formidable to match. The most significant are:

- **High-quality materials.** The best semiconductor materials, silicon and gallium arsenide, are routinely made with astonishing structural perfection. Even commercial silicon wafers are grown so that the most common impurity, an oxygen atom, occurs only once for every 50,000 silicon atoms. For specialized uses, silicon and other materials (notably gallium arsenide) can be produced in far higher purity. Furthermore, high-quality interfaces between semiconductors and certain other materials play crucial roles in these technologies. For example (as shown by atomic resolution imaging in Figure 7.2), a thin layer of silicon dioxide usually acts as the “gate oxide” in a modern field-effect transistor. The interface between gallium arsenide and aluminum gallium arsenide is critical to the creation of nearly ideal two-dimensional electron gases, the basis for many scientific discoveries such as the integer and fractional quantum Hall effects.

- **Flexible fabrication.** Semiconductors can be manipulated spatially with remarkable precision. They can be grown by successively depositing one atomic layer at a time and with varying composition. They can be patterned within the growth plane by a variety of lithographic techniques with sub-micrometer resolution.

- **Simplicity.** Semiconductors behave electronically with almost an ideal simplicity. For nearly all purposes, the microscopic complications of the crystal lattice of nuclei and an even higher density of electrons interacting together quantum mechanically can be ignored. Instead, the materials behave like a featureless “vacuum” in which small quantities of particles of negative and positive charges—electrons and holes—behave as they would in free space, provided that one only treats their mass as an effective parameter characteristic of the material and includes a dielectric constant that partially screens their Coulomb interactions. This simplicity makes understanding and modeling semiconductor behavior relatively easy and reliable.

- **Sensitivity.** Along with the above factors, which highlight the robustness of semiconductors, they also exhibit a complementary sensitivity to small changes of parameters. For instance, the conductivity of a semiconductor can be modified by many orders of magnitude by the introduction of small controlled concentrations of specific impurities (doping), and by the application of electric fields using nearby metallic electrodes (gating). This sensitivity is essential for the usefulness of semiconductors, since it is precisely such modulation of their properties in space and time that allows devices to function. For example, the conductivity of a field-effect transistor is controlled by modifying a voltage on a gate electrode. The science of this sensitivity is a result of specific materials properties characteristic of semiconductors: a large dielectric constant, a small effective carrier mass, and a small band gap.

For another material to supplant semiconductors, even for specialized applications, it must overcome at least one of the limitations of semiconductor materials while remaining cost-effective. What are these limitations? One is a practical limit on the minimum feature size in a semiconductor. As mentioned above, since electrons and holes in a semiconductor behave like particles in free space, the basic electronic unit is just an “effective atom,” whose size is simply its effective Bohr radius. Because of the same properties that make their modeling and manipulation simple—small effective carrier mass, large dielectric constant, and small band gap—this Bohr radius is typically large compared to true atomic scales. In silicon and gallium arsenide, for instance, the effective Bohr radius for electrons is approximately 45 and 190 times larger, respectively, than the true Bohr radius of the hydrogen atom. The volume inside this bound state contains many
thousands of atoms. Thus there is much room for improvement, in principle, by shrinking the size of these effective Bohr radii.

Another limitation is functionality. Because the ground state of a semiconductor is rather featureless, basically the only degrees of freedom available are those of artificially induced (extrinsic) electrons and holes. These are dilute and mainly suitable for controlling the charge density. There is notably no intrinsic magnetism or significant displacement of the atomic lattice. Magnetism (correlation of spins) and ferroelectricity (correlated displacements in the atomic lattice) are key features that enable other types of phenomena and technologies. They are of course used already in a variety of applications, but not with anywhere near the same flexibility as found in semiconductor processing.

**What Are the Unique Capabilities of Correlated Materials?**

Strongly correlated electronic materials are promising candidates to provide new functionality, which cannot be found in semiconductors, in part because they exhibit complex types of ordering. Emergent properties of correlated electron materials include ferromagnetism, antiferromagnetism, unconventional and high-temperature superconductivity, charge- and orbital-density waves, electronic phase separation, stripes, ferroelectricity, colossal magneto-resistance and magneto-capacitance. Obtaining even one of these properties in conventional bulk semiconductor materials is difficult, although correlations can become much stronger in semiconductor heterostructures at low temperature. The tendency for ordering even at room temperature in correlated materials results from strong Coulomb interactions between electrons confined tightly in d or f orbitals. The small size of these orbitals also means that many phenomena vary over distances much shorter than the large effective Bohr radii encountered in semiconductors, potentially allowing smaller electronic devices in correlated materials.

A second reason to look to correlated materials is their ability to respond sensitively to small perturbations. As discussed above, such sensitivity is critical to the broad utility of semiconductors. In semiconductors, this ultimately results from the small binding energies and large sizes of impurity states (the “effective atoms” that contribute electrons to the device) and their small band gaps. Other weakly correlated materials, which are metals or strong insulators, are much less sensitive, either (as in metals) having so many intrinsic charge carriers that their number can be only negligibly modified, or (as in insulators) having such a large gap and large impurity binding energies that these cannot be controlled. A semiconductor lies between these two extremes and in a sense achieves its exquisite sensitivity because it is close to the transition between metallic and insulating phases.

Strongly correlated materials very often show strong sensitivity to small perturbations for a similar reason: they are “close” to several different types of ordered phases. For instance, in materials known as Mott insulators, Coulomb repulsion forces a fixed number of electrons to partially fill an atomic shell on each atom, leaving undetermined the spin and orbital state of these localized electrons. The secondary effects of kinetic energy, magnetic exchange, and coupling to distortions of the ionic lattice are necessary to pick out the ultimate phase. As a result, there are often several rather different electronic phases that are quite close in energy, and which one is chosen is decided by very small changes in material parameters. This physics is important both for high-temperature superconductors and for certain magnets (see Sidebar “Frustrated Magnetism”). Different electronically ordered states can even coexist in the same material, as for example in materials that combine superconductivity and magnetism, traditionally thought to be mutually exclusive.

**Why Are Correlated Materials Challenging?**

Research on correlated materials is not completely new. For instance, the concept of an antiferromagnet—a material in which electrons are localized on atoms by strong Coulomb repulsion and their spins arrange themselves in a regular but non-uniform pattern—was recognized in the 1930s, and was confirmed experimentally by neutron scattering in 1949. However, the breadth of phenomena in correlated materials and their relative complexity in comparison to semiconductors means that today, both the understanding of strongly
Frustration—the Presence of Competing Interactions that Cannot be Simultaneously Optimized—Leads to Correlated Materials Whose Properties Can Be Controlled by Very Small Chemical Changes

The spinel structure is one of the most common mineral forms. It is composed of three types of atoms with the generic chemical composition AB₂X₄. Usually, the A and B atoms are metals, and the X is a chalcogen (oxygen, sulfur, or selenium). When the structure is magnetic, spins can reside on either or both of the A or B sites. Taken alone, the A sites form the well-known diamond lattice, while the B sites form the so-called pyrochlore lattice (Figure 1).

The pyrochlore lattice is a network of corner-sharing tetrahedra. It is one of the most frustrated geometries for antiferromagnetism (neighboring spins are antiparallel) because it contains many triangular faces, and three spins on a triangle cannot all be antiparallel (Figure 2). Spinel magnets illustrate the diversity of behavior of frustrated systems, as well as their sensitivity to small changes in parameters. Three examples are discussed here; in all cases the B atom is chromium, which in its preferred Cr³⁺ state creates a frustrated pyrochlore lattice of isotropic spins.

When the A atom is non-magnetic, A = zinc (Zn), cadmium (Cd), or mercury (Hg), and the X atom is as small as possible, X = oxygen (O), the distance between magnetic Cr spins is minimized, and their direct exchange coupling dominates their behavior. These materials are beautiful examples of nearly ideal “Heisenberg” pyrochlore antiferromagnets. They exhibit strong frustration, which is relieved by their coupling to the lattice, so that their low-temperature antiferromagnetic ordering is accompanied by strong lattice distortions. The strong correlations in their “spin-liquid” state above the ordering temperature have been observed directly in CdCr₂O₄ by neutron scattering (Figure 3). Interestingly, these three materials all order differently, giving further evidence of the sensitivity of strongly correlated materials to perturbations, in this case minute differences in the magnetic and lattice interactions induced by changing the A atom.

If the non-magnetic A atom is replaced by a magnetic one, e.g., A = cobalt (Co) or iron (Fe), the materials become ferrimagnetic, i.e., show coexisting ferromagnetism and antiferromagnetism. The antiferromagnetism in CoCr₂O₄ has a spiral character. This induces an electric polarization, and the two are strongly coupled. Indeed, recent experiments have demonstrated control over the electric polarization by magnetic manipulation of the magnetization.
If instead, the A atom remains non-magnetic, but the X atom is replaced by a larger S or Se atom, the lattice is expanded and the distance between Cr spins increases. In these materials, the magnetic exchange is believed to no longer be dominated by direct coupling between the Cr spins, and the resulting behavior is much more complex. Just as magnetic frustration can induce lattice distortions, it can also couple to the electrical polarization and dielectric constant. In CdCr$_2$S$_4$, a strong spin-lattice coupling gives rise to a “colossal magneto-capacitance,” an approximately five-fold increase in the dielectric constant upon application of a relatively small 5-Tesla magnetic field.

**FIGURE 3.** The intensity of scattered neutrons in CdCr$_2$O$_4$ (shown by color scale) as a function of momentum.

SOME KEY PROBLEMS IN CORRELATED ELECTRON MATERIALS

**High-Temperature Superconductivity**

The family of superconducting cuprate materials, which have fascinated and perplexed the community since their discovery in 1986, provide a paradigmatic example of strongly correlated materials. These materials have increased the highest temperature at which superconductivity occurs in solids more than fivefold, to 138 K (at atmospheric pressure). High-temperature superconductivity remains one of the defining problems for quantum condensed-matter physics. These materials have catalyzed a rich variety of experimental advances, from crystal and film growth to high-resolution photoemission spectroscopy and diverse scanning-probe microscopies, and they have led to a similar improvement in theoretical techniques. As a result, these materials and their superconductivity are much better understood.
understood today than a decade ago, and an ever more
detailed understanding is emerging year by year. De-
spite these successes, the key puzzles of the cuprates re-
main unresolved. When they are resolved, it should be
possible to design superconductors that work at higher
temperatures, possibly even reaching room temperature.
If room-temperature superconductivity is achieved, it
will truly and totally transform many technologies from
transportation to power generation and distribution to
imaging.

The greatest practical and fundamental questions in
high-temperature superconductivity are related: How
high can one push $T_c$ (the temperature below which the
material is superconducting)? What is the mechanism
for the superconductivity? A rational approach to the
former requires an answer to the latter, which we still
lack. The question of the mechanism is an intriguing
one, especially this year, the 50th anniversary of the
seminal paper by Bardeen, Cooper, and Schrieffer
(BCS) reporting their very successful theory of what are
now called conventional low-temperature superconduc-
tors. The BCS paper provides a benchmark for what a
successful theory should provide: an explanation of how
superconductivity evolves out of the “normal” (i.e., non-
superconducting) state that is found above $T_c$ and a
model for the mechanism.

Comparison to the BCS theory highlights the major
theoretical quandary of high-$T_c$ superconductivity.
The normal state of the cuprates, unlike that of con-
ventional materials, is itself a poorly understood
“strange metal.” In truly normal metals, like the copper
used in house wiring, electrons show no significant
correlation beyond what is imposed by their quantum
(Fermi) statistics. Such metals are known as Fermi
liquids after Enrico Fermi, who first identified how an
assembly of a large number of independent electrons
should behave. In contrast, the electrons in the strange-
metal state are strongly correlated despite remaining
liquid and repeatedly defy the expectations for a
Fermi-liquid metal.

A theory of the strange metal is likely to be a key
component in any successful theory of high-tempera-
ture superconductivity itself because it is out of the
strange metal that the superconductivity arises. Since
the identification of the strange metal in the cuprates,
similar metallic “non-Fermi-liquid” behavior has been
found in other electronic materials, lending further
significance to the problem. While there are some
exciting ideas and approaches to the problem—with
exotic names like quantum criticality, marginal Fermi-
liquid theory, and dynamical mean-field theory—
understanding the strange metal is a significant
challenge to the physics and materials communities.

Most recent work on the cuprates centers on one
part of the strange metal region of the phase diagram,
known as the pseudo-gap regime. In this regime, mate-
rials are being pushed away from the optimal supercon-
ducting state toward the Mott insulator mentioned
earlier—a fundamentally different state of matter that
is insulating not because of band structure but because
of interaction-induced electronic correlations. As
described above, proximity to a Mott insulator seems
to be a common source of complex behavior in quantum
materials. Indeed, the full complexity of the pseudo-gap
regime of the cuprates is only now beginning to be re-
vealed. Early studies based on standard probes observed
only that there seemed to be a gradual reduction in the
number of low-energy excitations; the current name for
the state is based on the similarity between these obser-
vations and the excitation gap of a superconductor.
However, in the early years of high-temperature-super-
conductivity studies, this region of the phase diagram
could only be studied to a limited extent, owing to the
lack of high-quality samples at low doping and of
appropriate experimental probes. As a result of a
Herculean effort by the community, this situation has
dramatically changed, and both crystals of remarkable
quality and a diverse range of high-resolution tools are
now being employed to study the problem (see Sidebar
“High-Temperature Superconductivity”). They have
revealed an unanticipated diversity of phenomena.

Experiments on the pseudo-gap state have uncovered
clear examples of coexisting electronic orders—usually
referred to as “competing orders” in this community.
Perhaps most dramatic are the scanning tunneling
microscope images, which have shown intrinsically in-
homogeneous energy spectra (Figure 4.4) and strong
evidence of short-range electronic charge ordering. Such
HIGH-TEMPERATURE SUPERCONDUCTIVITY

Study of High-Temperature Superconductivity Has Revealed Exciting New Physics and Stimulated Advances in Electron Spectroscopy

High-temperature superconductivity in the cuprates rocked the scientific community upon its discovery in 1986 and has remained a major challenge to our understanding ever since. The occurrence of superconductivity—the flow of electric current without resistance—in such unconventional materials (ceramics instead of metals) at such high temperatures (the record at atmospheric pressure is $T_c = 138$ K, as compared to typical values of $T_c \approx 10$ to 15 K in conventional materials) stimulated enormous scientific activity. As it became clear that a quick explanation would not be forthcoming, the importance of the problem led to steady development of difficult experimental techniques and improved materials. These advances facilitated scientific and technological progress much more broadly. Probably the techniques that have benefited most from two decades of high-$T_c$ research are spectroscopic probes of electrons: angle-resolved photoemission and scanning tunneling spectroscopy.

Angle-resolved photoemission spectroscopy (ARPES) is a technique to measure the distribution of energy and momentum of electrons in a material. High-intensity radiation (light) illuminates the sample. A photon absorbed by an electron gives the electron enough energy to escape from the crystal. By measuring the energy and momentum of the ejected electron and knowing these quantities for the incident photon, one can deduce the energy and momentum of the electron before it was scattered. Primarily because of the demands of the cuprates, the energy and angular (hence momentum) resolutions of ARPES have improved by roughly a factor of 100 and 20, respectively! In the cuprates, ARPES has allowed direct measurement of electronic scattering rates, Fermi surfaces, angular variation of the gap, and coupling of electrons to collective modes (see for example Figure 1). It is being applied much more broadly, to characterize novel materials such as Sr$_2$RuO$_4$, graphene, MgB$_2$, heavy fermion and organic superconductors, and many others.

Development of several scanning probe techniques has been spurred by efforts to understand high-temperature superconductivity. These techniques enable an experimentalist to scan the surface of a sample and record many different properties, including local electronic structure, magnetic field, charge density, compressibility, and others. To make the dramatic observation shown in Figure 2 requires stabilizing the STM and sample at a much-elevated temperature compared to the 4.2-K norm for these sorts of measurements.

![Figure 1](image1)

**Figure 1.** An image of the Fermi surface of the high-temperature superconductor Bi$_2$Sr$_2$CaCu$_2$O$_{8+x}$ reconstructed from ARPES data.

![Figure 2](image2)

**Figure 2.** Scanning tunneling microscope (STM) data on a high-temperature superconductor, demonstrating large local variations of the energy gap (energy required to add or remove an electron). The area shown is 30-nm square, and the color scale varies from a gap of zero (white) to approximately 100 meV (black). Remarkably, this data was taken at 120 K, well above the 93 K superconducting-transition temperature of this sample. Clearly some sort of gap persists into the normal state!
fluctuating charge order is present both below and above the superconducting critical temperature, $T_c$. Other experiments—nuclear magnetic resonance, muon spin resonance, and inelastic neutron scattering—have provided evidence for magnetic fluctuations and/or local magnetic ordering as well, even coexistence of antiferromagnetism and superconductivity.

Stimulated by experiments like these, both in the cuprates and in other quantum materials, theory seems to be converging on the notion that competing or coexisting orders are often the cause of emergent behaviors such as high-temperature superconductivity. This notion is also relevant to other superconductors, such as those based on the heavy-fermion compounds and organic materials. The key elements to understand are the nature of the competition and the relation between these orders, which would lead to a unifying description. This understanding would permit the community to model and calculate properties of materials in this regime. This challenge to theory remains open, and though there are ideas, they are controversial. Both new experiments and more theoretical work will be needed to elucidate the situation, followed by ideas for the creation of new, higher-performance materials.

**Correlated Quantum Liquids**

High-temperature superconductivity, with its non-Fermi-liquid normal state, focused attention on a significant technical advance. STM measurements of high-temperature superconductors have separately identified and mapped the distributions of different types of impurities, dopants, and superconducting vortices; spectroscopically characterized the different electronic states; and revealed emergent spatial structures, such as checkerboard and stripe correlations. STMs and other scanning probes provide a powerful general tool to measure and manipulate a host of nanoscale structures and are used across an increasing number of scientific disciplines.

**FIGURE 4.4.** Spectroscopic imaging with atomic-scale spatial resolution is now possible. *Left:* Atomic-resolution scanning tunneling microscope image at 4.2K of BiSrCaCuO, a high-temperature superconductor (see Figure 1 in sidebar “High-Temperature Superconductivity). *Right:* A map of the superconducting gap. Since most chemical reactions start at surfaces, these images also hold the key to understanding the relationship between electronic and atomic structure in condensed matter.
correlated quantum liquids more generally. It is now recognized theoretically and experimentally that unconventional quantum fluids arise in many guises. An interesting example is the thermoelectric (a material that generates an electrical voltage from an applied temperature gradient) Na$_x$CoO$_2$, which has a very large thermopower for a sodium concentration $x > 0.75$ and may be useful in low-temperature refrigeration applications (Figure 4.5). The high thermopower is directly related to strong correlations, which lead to a large spin entropy transported by the charge carriers. Effective room-temperature thermoelectrics have been made in superlattices combining two strongly correlated oxide materials, made using methods described later in this chapter.

Correlated liquids also occur in insulators, in which case the correlated particles are neutral, e.g., spins rather than charges. Examples of spin liquids are continually accumulating as more and more compounds with frustrated magnetism are being synthesized and studied (see Sidebar “Frustrated Magnetism”). A very exciting prospect, envisioned by Philip Anderson as early as 1974, is the idea of a quantum spin liquid, in which the combination of frustration and quantum zero-point motion are sufficient to suppress magnetic order, even at zero temperature (absolute zero).

More than 30 years later, a number of very promising materials exhibiting such behavior have just recently begun to appear: ZnCu$_3$(OH)$_6$Cl$_2$, called herbertsmithite, a layered material whose spins become correlated below 300 K, the so-called “Curie-Weiss temperature,” but which does not order even at the lowest measured temperature of 50 mK; Na$_4$Ir$_3$O$_8$, where the Curie-Weiss temperature is greater than 600 K and there is no order above 2 K; and several other organic and inorganic materials. Theory suggests that quantum spin liquids can exhibit quite remarkable properties, such as artificial photons—propagating excitations that behave just like light in a dielectric but are different from true electromagnetic waves—and fractional quasiparticles with exotic quantum statistics, which could in principle be an error-free foundation for quantum computing. Connecting the experimental examples to the theoretical proposals is a difficult challenge, but one with great intellectual and practical potential. In general, understanding quantum liquids is a key fundamental scientific issue in correlated materials.

**Coupling Spin and Charge**

Numerous new technologies could be enabled by materials in which charge-related properties—charge density, electric polarization, and currents—interact with spin-related (magnetic) ones—magnetization, spin currents, and spin waves. A simple example of an exciting device based on these phenomena is a giant magneto-resistance (GMR) spin valve, in which the electrical resistance is modulated by the orientation of a magnetic domain in a metallic material. Such GMR devices are already quite successful technologically for high-density information storage and represent a several-billion-dollar industry. Correlated electron materials offer many other means in which spin and charge can become coupled.

The colossal magneto-resistance (CMR) manganite materials display much larger resistance changes than GMR devices even within a single material. So far, their applications have been limited by materials properties and the fact that the CMR phenomena peaks
below room temperature. However, the fundamental science of the manganites remains a fascinating subject with many open questions and presents a stimulus for new materials synthetic research. Many manganites display microscopic phase separation, but it is not known whether this is intrinsic or critical to the CMR. Some manganites are “half-metallic” ferromagnets, which means that only one spin polarization conducts, while the other is insulating. Since the current is then spin-polarized, this may be useful to inject currents of electron spin into other materials.

Other manganites behave as multiferroics at sufficiently low temperature. A multiferroic is a material that is simultaneously magnetic (sometimes exhibiting ferromagnetism and sometimes not) and ferroelectric. Similarly to a ferromagnet, which has a spontaneous magnetic dipole moment, a ferroelectric has a spontaneous electric dipole moment or electric polarization, usually as a result of a rearrangement of atomic ions in the crystal structure. Ferroelectrics are used in diverse applications from barbeque lighters to motion sensors and non-volatile memory for data storage. The combination of ferroelectricity and magnetism is, however, quite rare. When present, it can be an impressive example of correlation physics: magnetism arises from electron correlation, while ferroelectricity from correlation of charged ions, i.e., of the crystal lattice. Only recently have new classes of such multiferroics have been discovered, and an understanding of the interplay of these two types of orders has begun to be developed (see an example in the Sidebar “Frustrated Magnetism”). In some of these promising new materials, magnetism and ferroelectricity are strongly coupled. The prospect of multiferroic materials with strong magneto-electric coupling is also exciting from the point of view of applications, potentially allowing (see Figure 4.2) electrical control of magnetism, e.g., for information storage technology.

**Correlations in Heterostructures**

While we have emphasized that correlations in conventional semiconductors are ordinarily weak, much stronger correlations appear in semiconductor heterostructures (artificial structures of two or more materials). As a result of their many applications, semiconductors have been the subject of vast R&D investments aimed at developing materials of unprecedented purity and structural quality, as well as methods to process them with exquisite control, in order to optimize device performance and production yields. These investments have also paid off for fundamental science in a number of ways and will continue to do so. More recently, major progress has been made, largely outside the United States, in fabrication of high-quality heterostructures made from strongly correlated materials. These strongly correlated heterostructures (see Sidebar “Correlated Interfaces”) can be used to create devices that surpass some limitations of current semiconductor devices.

Several remarkable examples of electronic correlations were discovered via the creation of nearly ideal two-dimensional electron gases (2DEGs) at the interfaces between GaAs and AlGaAs. In low-temperature experiments, such 2DEGs have provided the setting for the observation of the integral and fractional quantum Hall effects (which reflect complex correlated states that appear in high magnetic fields) and for the observation of quantum-interference effects such as weak localization. When further confining potentials are applied within the plane of such a 2DEG, lower-dimensionality structures are created with high reproducibility. This has given rise to the observation of conductance quantization in narrow constrictions (quantum point contacts), and Luttinger–liquid behavior (a kind of one-dimensional strange metal) in quantum point contacts, and quantum wires, and a great variety of effects. In quantum wires and quantum dots—fully confined structures in which the number of electrons can be precisely controlled—effects such as the Coulomb blockade and the Kondo effect (both discussed in Chapter 6) and the quantum manifestations of classical chaos have been observed.

The GaAs/AlGaAs 2DEG will remain a key platform for fundamental physics research in the foreseeable future, because of its availability, flexibility, and quality. For these reasons, it is one of the best systems to explore controllability of electronic quantum correlations, one possible application of which would be quantum information processing. Some of the most challenging problems in this direction are:

- Control and manipulation of individual electron spins. In quantum-dot structures, it has been shown possible to manipulate and measure the
Interfaces between Correlated-Electron Materials—the First Step toward Semiconductor-Type Heterostructures—Have Been Made and Show New Behavior Not Found in their Semiconductor Counterparts.

Experimenters in recent years have been taking the first steps toward semiconductor-style heterostructures (devices made by using precisely spatially modulated chemistry) grown from correlated electronic materials, involving d or f electrons. Ultimately, such devices might allow one to combine the flexibility of semiconductor processing with the added capabilities of these materials due to collective phenomena like magnetism or superconductivity. In fact, the latest experiments show that these devices can show even more functionality that does not show up in bulk materials.

Consider a structure consisting of SrTiO$_3$ (dark layers) and LaTiO$_3$ (bright layers) taken by scanning transmission electron microscopy (Figure 1). In bulk crystalline form, SrTiO$_3$ is a “band insulator” with unusual dielectric properties, while LaTiO$_3$ is an antiferromagnetic strongly correlated Mott insulator. Remarkably, charge transfer between the two materials results in a conducting two-dimensional electron gas at the interface, despite the fact that both materials are insulators.

Other interfaces of this type are under increasing investigation. The interface of SrTiO$_3$ and LaAlO$_3$, two correlated band insulators, also gives rise to a conducting interfacial electron gas. In this case the measured conductivity indicates a very high quality. The carrier mobility, the velocity induced per unit applied electric field, was higher than 10,000 cm$^2$/Vs, comparable to good quality electron gases in GaAs.

Very recent experiments suggest that the interface between SrTiO$_3$ and LaAlO$_3$ is not only conducting, it is also magnetic. Even more so than the conductivity, this is surprising since neither material is magnetic. Figure 2 shows hysteresis in the sheet resistance of the interfacial electron gas, strikingly similar to that seen for ferromagnetic metals. It is likely that, as proposed by the experimenters and supported by theoretical calculations, electrons are transferred at the interface into the Ti $d$ orbitals. Then, because of the strong Coulomb repulsion in these orbitals, they become correlated and magnetic. Other signs of classic correlation phenomena like the Kondo effect were also observed in the same study. It is intriguing to consider the possibilities of combining ferromagnetism and two-dimensional electron transport in this structure, which is completely different from the diluted magnetic semiconductors that have been intensively studied in the last decade.
Another very different effect is observed in a related but distinct structure: an electron gas localized about a single unit-cell-thick layer of SrTi_{0.8}Nb_{0.2}O_3 embedded inside bulk SrTiO_3. This electron gas was found to show an enhanced thermoelectric effect, i.e., generation of a voltage by a temperature gradient. Its Seebeck coefficient—the ratio of the induced voltage to the temperature gradient—was observed to be approximately five times larger than in bulk SrTiO_3 (see Figure 3). Such large values could make these kinds of structures useful in diverse thermoelectric applications.

Activity on correlated electron interfaces in on the increase, though almost all fabrication of these structures is taking place outside the United States. Given the richness of collective phenomena in correlated materials, the spectrum of science to be explored in such layered structures is almost limitless.

Along with continued exploration of semiconductor heterostructures, heterostructures fabricated from two or more strongly correlated materials provide a very powerful path to devices in which spin, charge, and atomic structure are intricately interwoven and can be controlled independently. These are already leading to improvements of materials such as thermoelectrics, in which optimization requires independent control of thermal and electrical transport properties.

**CORRELATION PHENOMENA BEYOND ELECTRONS**

**Ultra-Cold Atomic Gases**

The last decade has witnessed several remarkable experimental advances in trapping and cooling ultra-cold atomic gases to extremely low temperatures (microkelvin or even nanokelvin). The interest in doing research on ultra-cold atoms has skyrocketed, and the manipulations of the trapped atoms are increasingly sophisticated. So far, the majority of experiments in these systems has focused on condensates, a quantum phenomena in which, as in a superconductor, a macroscopic number of particles occupy a single quantum state extending over the entire atomic cloud (see the discussion of coherence in Chapter 2).

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**FIGURE 3.** Plot of the absolute value of the Seebeck coefficient shows that the two-dimensional electron gases at the interface (2DEGs) have an enhanced thermoelectric effect relative to bulk SrTiO_3.

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For bosonic atoms, quantum degeneracy leads to Bose–Einstein condensation, similar in general terms to the superfluid transition in $^4$He. For fermionic atoms, quantum degeneracy and atomic interactions lead to a condensate of Cooper pairs of atoms, in the same way as electrons form Cooper pairs in a conventional superconductor. The tools of atomic physics discussed in Chapter 2 can be used to manipulate these states in ways that are impossible with either liquid helium or superconducting solids. One example is that the superfluid state made from fermionic alkali atoms can be tuned continuously between a Bose condensate of diatomic molecules and a Cooper-paired state analogous to superconductivity. Another is that superfluids of bosonic atoms with spin ("spinor Bose condensates") can be tuned between states that combine magnetic and superfluid order in different ways.

A trend for the future in this field is a move from "simple" condensate formation toward situations in which the atoms are strongly correlated. This can be accomplished by suppressing kinetic energy with an optical potential; it can also be done by strengthening inter-atomic interactions by tuning to an atomic “Feshbach resonance” or using dipolar atoms with long-range interactions. A significant community is developing at the interface of condensed-matter and atomic physics, combining the theoretical expertise in correlation physics from the former with the experimental methods and quantum information perspective of the latter. The result is an ever-increasing ability to control quantum correlations in these systems. This is possible because the atoms in these systems are so well separated that their internal quantum states remain largely unmodified by their environment and thus can be well understood and precisely controlled through laser excitation. Another significant advantage is that it is frequently easier to observe the real-time quantum dynamics in these systems than in solid-state materials because they are so much slower.

A major effort for the future is the creation of optical lattice emulators, in which challenging problems in correlated electron physics are attacked by building atomic analogues. An optical lattice created by interference of laser beams is used to replicate the lattice of a...
solid by trapping atoms preferentially at the lattice points. A precisely engineered atomic system could, for instance, answer the still controversial question of whether the Hubbard model (a popular starting point for theory of high-temperature superconductivity) contains the right physics to describe the cuprate materials. Ultimately, such quantum emulators could address a multitude of problems in which ordinary computational studies are prohibitively costly. By engineering systems with interactions different from any crystalline material, it may also be possible to produce novel quantum states with properties not found in solids but desirable from a fundamental scientific or a technical point of view. For example, one might be able to produce conjectured “topological” states of matter whose exotic excitations encode information in a highly non-local way useful for encryption or computation.

The key challenge in progressing toward the above goals is developing new probes and trapping methods for ultra-cold atoms. Currently most of the probes used to determine the state of an ultra-cold atomic gas are not directly comparable to the standard probes used to determine correlated structure in solids. For example, rather than directly measuring momentum-space properties as in neutron or photon scattering in solids, atomic physicists measure the momentum distribution destructively by releasing the condensate, allowing the atoms to strike a distant screen, and interpreting the real-space distribution on the screen to provide information about the original momentum-space distribution. This method is sufficient to determine basic properties such as superfluidity; however, advances in measurement would enable many more quantitative comparisons between electronic and atomic systems.

**Soft Matter**

The ubiquity of strong correlations is not limited to quantum phenomena in hard inorganic and organic crystalline solids. Indeed, complex structures and behaviors appear with great regularity in soft materials, which we take to mean materials built from particles larger than atoms or small molecules, e.g., organic constituents, polymers/macromolecules, or even micron-sized particles or grains (see Chapter 3). Strong correlations can be induced by the geometric constraints from the connectivity of the large particles involved, by strong electrostatic interactions of ionized constituents, or by hydrodynamic effects of the fluids involved. Because the characteristic interaction energies are also significantly lower and often comparable to the available thermal energy at room temperature, thermal fluctuations are more significant, and quantum effects are usually negligible.

*Equilibrium correlations in soft matter.* Problems in soft matter are very diverse, reflecting the strong interdisciplinary nature of the field and interactions between the scientific and engineering communities in these areas. An interesting and important example with broad relevance is the physics of screening in ionic fluids. Many important structures in biological systems are significantly charged in the cellular fluid. For example, DNA carries a (negative) charge of approximately 1 electron per 3 Ångstroms of its length. However, the DNA must often condense into a very compact form, which requires screening of this charge. Remarkably, under many circumstances, over-screening can occur, resulting in an effective net attraction between like-charged objects (see Figure 4.7) such as DNA or actin filaments! It can be shown that if there are no correlations between the ionic screening charges, such attraction is impossible, and generally it is believed that such attractive forces are the result of highly correlated screening layers very close to the structures being attracted. An understanding of such correlated screening

![Figure 4.7](image_url)
in a sufficiently general context to be useful to biologically relevant modeling or design of drug delivery systems is a great challenge to theory and experiment.

Non-equilibrium soft matter. Because the molecular building blocks of soft matter are much larger than atoms, generally the microscopic “rearrangement time” is much longer than in hard materials. Moreover, all motions are essentially classical. Without quantum tunneling, the molecules cannot pass through energy barriers in their motion, but must pass over them by thermal activation, which is often a slower process than in hard materials because of the longer rearrangement time. When strong geometrical constraints are present, this longer rearrangement time often leads to the material falling out of equilibrium. In the extreme case, when the particles involved are large compared to atomic or molecular scales, for instance grains in a sand pile, the forces between them can be so strong that thermal agitation is completely negligible, and the system is never even close to equilibrium (see the discussion of “jamming” in Chapter 6).

This general class of phenomena is of great fundamental and practical importance. Structural glasses, materials that exhibit a shear modulus like a solid but are amorphous rather than crystalline, are extremely common over a wide array of chemical constituents, ranging over silica (window) glasses, metallic glasses, polymer glasses, and a variety of soft materials made from larger constituents like polystyrene spheres (see Chapter 3). They exhibit behavior intermediate between that of solids and liquids, and respond to stresses non-linearly and over a tremendous range of time scales. For example, for some materials super-cooling through the glass transition yields a striking range of viscosities that vary a billion-fold over a narrow range of temperatures. The nature of this growth remains a challenge to understand. Failure modes—fracture, crack propagation, and plastic deformation—in amorphous and composite solids are critical to their performance, and their strength can often exceed that of similar crystalline solids. Understanding in this area is vital to improving the performance characteristics of the composite materials now used, for example, in the aerospace industry. Even empirical models for such behavior are not well developed. Advances in experimental probes, such as imaging of individual particle motions in these materials, when coupled with improvements in theoretical models, promise major progress in these important challenges over the upcoming decades. While there are many further examples of equal significance, we defer their discussion to Chapter 6, which focuses entirely on non-equilibrium phenomena.

Collective Phenomena in Biology

Many of the most challenging problems at the frontier of modern biology require understanding how complex collective phenomena emerge from a large number of relatively simple constituents. Certainly biological organisms, to function, involve correlated interactions of an enormous number of constituents. One feature distinguishing biological systems from the materials discussed earlier in this chapter is their complexity. For example, the number of distinct types of proteins in a cell typically is much larger than the number of distinct types of atoms in a non-biological solid. In addition, while correlated materials may involve several distinct length or energy scales, in biology this is carried to an extreme (see Sidebar “Correlated Biological Materials”). Finally, biological systems are always far from equilibrium (though in some limited situations some biological subsystems may be in local quasi-equilibrium). Thus, it is clear that understanding practically anything about functional mechanisms in a cell or in a higher-level structure from the microscopic degrees of freedom is a very challenging correlation problem! Until recently, this could be viewed largely as an academic observation. Now, with the dramatic advances in understanding the details of molecular biochemistry and bioinformatics, there may be sufficient microscopic knowledge that the problem of understanding the origin of collective phenomena in biological systems can be profitably studied.

At present, such a “mechanical” understanding of collective biological properties and processes is extremely limited. One area where significant progress has been made recently is the biophysics and biochemistry of single molecules. Tools such as “optical
CORRELATED BIOLOGICAL MATERIALS

Like many engineered systems, a signature of biological systems is the precise, repeatable placement of its constituents in complex working machines. Unlike engineered objects such as cars, however, biological systems self-organize, develop, and age following rules encoded by the physics and chemistry initiated by the complement of biomolecules, many already precisely arranged, in the zygote. While the basic physics that drives these processes is largely the familiar macroscopic and mesoscopic kinetics and thermodynamics that we are comfortable thinking about, the complexity of the interactions, their nonlinearities, and their inhomogeneities prevent us from understanding how the cooperation of the innumerable chemical processes in a single cell is elaborated into an adult animal.

There are processes, however, that have begun to be uncovered that translate Ångstrom-scale correlations in structure and dynamics to the macroscopic function of entire organs. One clear example is the quasi-periodic beating of the human heart (Figure 1). The heart itself is, of course, a central organ in the life of many creatures. Its structure and placement in the body of the animal is critical to its proper function, and even small defects can lead to non-optimal functioning of the organism and early death. The heart beats in a nearly periodic rhythm. However, far from being a simple oscillator, these rhythms can have a complex temporal and spatial structure. Different amounts of temporal and spatial correlation in the heart rate are indicative of different heart abnormalities and disease states.

FIGURE 1. Correlations propagating upwards to successively larger length scales and longer time scales result in a beating heart.
tweezers” are used to stretch single RNA molecules and understand their mechanical properties, which are related to their sequences. Measuring the work done in stretching the molecule rapidly, starting from an ensemble of initial conditions, enables an experimental test of the non-equilibrium work relations and remains an active topic of research in statistical physics (see the Sidebar “Fluctuation Theorems” in Chapter 6). Electrostatic phenomena have been studied (as described above in the soft-matter section) and may be related to the assembly of DNA and histones into chromosomes. The ratcheting action of muscle fibers is another active topic, in which the function of molecular motors called myosins are being studied. These are closely related to basic questions about nanoscale mechanics and statistical physics. Physicists and chemists are attempting to construct inorganic molecular motors that are as small, efficient, and robust as biological examples, and to quantify how close biological nanomotors are to fundamental limits implied by quantum mechanics and thermodynamics. Many other examples of correlations in biological sciences can be found elsewhere in this document, especially in Chapters 5 and 6, but the quantitative understanding of collective phenomena in biology is very much in its infancy.

WHAT ARE THE NEEDS?

To address the grand challenge of correlation phenomena, a concerted effort is required in three broad areas: materials synthesis, experimental measurement and control, and theoretical analysis. We will discuss each in turn below, with some specific examples. In all of these directions, it is important to recognize that truly fundamental challenges require non-traditional approaches that often develop gradually only by long-term research over an extended period. For example, as described earlier in this chapter, high-temperature superconductivity has been a very productive research area, but progress has occurred over a 20-year period through the hard work of steadily improving experi-
mental tools, materials, and theoretical techniques. While each step in this process has yielded its own dividends, it is the long view held by many key researchers that has enabled this field to progress. Progress in such frontier areas also requires collaborative, cross-disciplinary research modes.

Materials synthesis is a key enabler for advances in correlation science. The example of the physics of two-dimensional electron gases at semiconductor interfaces has already been highlighted. The pervasiveness of these materials in science and technology is a consequence of a long-term, largely industrial, effort to grow them with ultra-high purity and in diverse geometries, and this has paid enormous scientific dividends. To successfully study and take advantage of strong correlations requires a similar ability to "design" and grow the appropriate samples (with consistently high quality and often in single crystalline form) for a much broader range of materials. For instance, there are many types of probes whose full informative potential can only be realized on large, single-crystal samples. Notable examples are neutron and angle-resolved electron photoemission spectroscopy. Other phenomena only appear when the defects of the material are reduced below some critical concentration.

This type of materials development cannot be done "on the side." Rather, it requires a continuity of effort and expertise over many years to improve quality and overcome hurdles involved in the highly non-equilibrium processes needed to grow most interesting solids. As discussed in Chapter 3, non-traditional approaches to materials growth, including biologically inspired self-assembly schemes may ultimately lead to a step change in this area and should be explored in parallel with traditional materials-science methods. A discussion of how to address the need for improvements in crystal and heterostructure growth is given in Chapter 7.

An equally important requirement for unlocking the puzzles of emergent phenomena is the creation of new tools for measuring correlations in the laboratory. While some correlations, such as the alignment of spins in a ferromagnet, are easily identified by such macroscopic signatures as a spontaneous magnetic moment, others like the antiferromagnetic order discussed earlier in this chapter are more subtle and require specific tools to uncover them. Continued development of new and improved experimental probes for complex magnetism, including scanning probes and x-ray nanoprobe, remains critical to observing new types of correlations.

Some directions for such development are clear. Spectroscopy and scattering using photons (x-rays), neutrons, and electrons should be pushed to ever higher resolution in momentum, energy, and space for imaging. As discussed earlier, electron photoemission spectroscopy has advanced dramatically in resolution in the last two decades to the point where it can be used to directly measure the Fermi surface of low-energy electron excitations in a variety of materials. This can be directly compared with theoretical electronic structure predictions. Further enhancement of resolution will enable a fuller characterization of the photoelectron wave function and scattering rates. Scanning microscopies such as scanning tunneling microscopy (STM), atomic force microscopy (AFM), and others have enjoyed tremendous development in recent years. These now provide a probe of local electronic and atomic structures at surfaces of crystals, molecules, and other structures. Continued development of scanning probes such as chemically sensitive AFM and spin-polarized STM will allow even more detailed correlations to be measured with atomic precision. Another major direction is the development of optical methods to study real-time dynamics of fast quantum processes in molecules and solids (Chapter 2).

Improved theoretical methodology is a necessary partner to the above materials and experimental efforts. The ultimate goal of theory is to provide an accurate, predictive guide to the properties of materials and structures, both to enable rational design of new synthesis efforts and to explain fundamental mechanisms in natural systems. In strongly correlated situations, the full process of deducing macroscopic behavior from known microscopic laws—e.g., determining the magneto-electric response of a complex crystalline solid from the basic equations of quantum mechanics—is an extremely difficult problem.

In the realm of solid-state physics, the most common of such ab initio ("from first principles") methods is density functional theory in the local
density approximation (LDA). LDA and its many descendants are designed essentially to capture the electronic structure of energy bands and basic structural parameters. In weakly correlated solids, they are quite successful. While this is an impressive achievement, it is clear that LDA-derived methods have inherent difficulties in capturing strong electron correlations. Recent attempts to combine LDA with dynamical mean-field theory (DMFT) partially address this problem. Even with such advanced corrections, LDA-derived methods are best suited for situations in which there is really a single characteristic length or energy scale; that is, in which a relatively small volume of the solid suffices to approximately reproduce the properties of the whole. However, among correlation problems of greatest interest, this condition is often not the case, and there are coupled, physically distinct processes occurring on a broad range of energy and length scales.

For example, in most magnetic materials, the exchange interactions which couple localized electron spins (typically, 1-500 K) are orders of magnitude smaller than the widths of the energy bands closest to the Fermi energy (usually of order 12,000 K = 1 eV), which represent the relevant (kinetic) energies of the conduction electrons. Frustration, described earlier, can suppress ordering to even lower temperature. Frequently, the competition between different interactions in correlated electronic materials leads to ordering at temperatures much below electronic energy scales. Competing and coexisting orders as observed experimentally indicate that even physics on tens of nanometer scales can be quite distinct from that within a few crystalline unit cells in materials such as the high-\( T_c \) cuprates or the manganites. In semiconductors at millikelvin temperatures, new collective phenomena occur because of energy differences thousands of times smaller than the typical kinetic or potential energy of electrons. In all these cases, the more subtle nature of the low-energy physics requires the development of distinct and novel theoretical approaches of a more phenomenological nature. Such phenomenological studies are also important in providing unifying conceptual frameworks for new types of emergent behavior that cannot be obtained from ab initio methods and occur on scales that vary from the quantum world on up to macroscopic biological systems.

If one moves outside the realm of electronic materials, the examples of “simple” systems with only one characteristic energy or length scale are even scarcer (practically non-existent). Failure and plasticity in solids involve atomic-scale rearrangements, motion of large defects such as dislocations, grain boundaries, or cracks, and long-wavelength elastic waves. In biology, even a simple organism makes use of a vast hierarchy of interacting constituents from the DNA and proteins up to organs and tissues, and there is feedback from the largest scales (the organisms) to the DNA through evolution. Thus, in most correlation phenomena, theory must deal with the existence of important processes over a broad range of length and energy scales. It is not practical to expect a single theoretical or computational framework to derive all this behavior from first principles. Instead, it is critical for theory to embrace modeling on multiple scales, combining different tools to connect the distinct scales.

In electronic materials, this means combining results from LDA-type methods with phenomenological “effective-Hamiltonian” modeling to understand low-energy behavior. Even nominally simple effective models like the Hubbard model popular in studies of the high-temperature superconductors contain several distinct energy and length scales. Thus, even at this already reduced level of complexity, such problems may require a combination of approaches for their understanding. Recent developments of powerful “cluster” methods seem likely to describe much of the short-distance, high-energy physics. How this is connected to the ultimate low-energy behavior (e.g., transport properties, magnetism, and superconductivity) remains a largely open problem. It is important that these largely numerical methods—which, although considerably improved in recent years, remain inherently rather local—be carried out in concert with low-energy approaches that can properly describe global behavior.

Conversely, in most correlated electronic materials, the microscopic spin and orbital level structure is not

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obvious, and the interactions between them are even less so. Despite the deep puzzles therein, the high-temperature cuprates are a model of simplicity when compared with most correlated electron materials. Thus, phenomenological approaches need input from first-principles or quantum-chemical methods to find an appropriate starting point. Much more interaction and collaboration between the ab initio and strongly correlated electron communities is needed to face the major challenges in these materials.

**CONCLUSIONS**

In this chapter, we have reviewed the Grand Challenge of understanding and controlling strong correlations and collective behavior in the basic energy sciences. We have seen that correlation phenomena are integral to fundamental scientific issues throughout this area and that their consequences can be highly enabling for improved functionality of materials and other structures. Advances in materials synthesis, experimental tools, and theoretical analysis are required if we are to take on this Challenge with a reasonable probability of success.