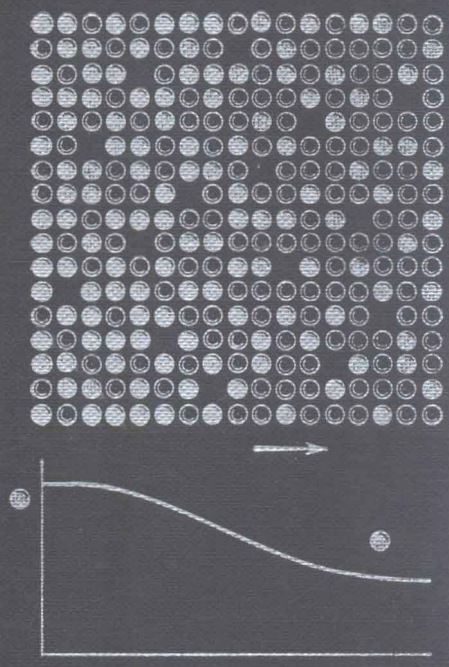

THE NATURE OF SOLIDS

ALAN HOLDEN

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FOREWORD

THIS BOOK provides to anyone who has studied physics or chemistry in a secondary school a nonmathematical account of how some of the behavior of solid matter is understood at present. Such a reader will find his prior knowledge rehearsed in early chapters and brought to bear on a few of the central questions raised by any penetrating study of solids. In later chapters he will learn why some of those questions cannot be answered in the terms usually taught in secondary schools, and he will meet the wave-mechanical pictures now used to answer them.

Necessarily this book gives a distorted view of the scientific adventure. Science was made by men, and men will continue to make it. Some of superior intellect and many more of ordinary ability have constructed the edifice patiently—making mistakes and correcting them—adding bricks, some marked with their names and others anonymous. The history of their efforts must be read elsewhere.

So too must any adequate description of the evidence for the pictures that this book presents. Like all scientific theories, they derive their final support from facts, often observable only in experiments ingeniously contrived to confirm or deny the theories. Only a few hints, however, of the interaction between theory and experiment appear in these pages. Instead they are devoted to explaining the theories—to picturing the models—that provide the best means known today for unifying our knowledge of solids and connecting it with broader fields of science. The study of that knowledge is commonly divided between the specialties of physicists, chemists, and crystallographers. Bringing together here their separate ways of speech may help to make clear the unity to which the scientific effort aspires.

ALAN HOLDEN

Murray Hill, New Jersey
January, 1965

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I. THEORIES

We make to ourselves pictures of facts.
LUDWIG WITTGENSTEIN,
Tractatus Logico-philosophicus

FORTUNATELY we have no trouble walking through a gas: air yields easily. A liquid looks more forbidding, and you will find it so if you jump into a pool and land flat on your stomach. But many a baby, confident that he can walk on water, is dismayed to find that it lets him down.

A solid gives a wholly different account of itself. It is rigid, and in order to get through it, you must hit it hard enough to break it. Once broken, a solid, unlike a liquid or a gas, stays broken. But to break it enough to walk among the pieces, as you would walk in a liquid or a gas, would take a great deal of pounding.

Such facts impressed Sir Isaac Newton sufficiently to draw from him a memorable demand:

> The Parts of all homogeneal hard Bodies which fully touch one another, stick together very strongly. And for explaining how this may be, some have invented hooked Atoms, which is begging the Question . . . . I had rather infer from their Cohesion, that their Particles attract one another by some Force, which in immediate Contact is exceeding strong, at small Distances performes the chymical Operations above-mention'd and reaches not far from the Particles with any sensible Effect . . . . There are therefore Agents in Nature able to make the Particles of Bodies stick together by very strong Attractions. And it is the Business of experimental Philosophy to find them out.*

**Optics* (1704).

Before experimental philosophy could undertake Newton's "business," much other work had to be done. Heat and light, just as familiar as solids, were just as mysterious. Few men recognized the existence of electricity other than lightning. Two centuries elapsed before the emerging physical and chemical scheme for interpreting Nature could begin to offer a penetrating response to Newton's challenge.

By that time many other properties of solids nagged the curious as much as their cohesion did. Why are some solids transparent and others opaque, some electrical conductors and others insulators? Why will some absorb much heat and others little? To describe these properties—to measure them and affix numbers to them—only sharpened the appetite to explain them.

There emerged two distinguishable ways of setting out to explain the behavior of solids: the *macroscopic* way and the *atomistic* way. Today these two ways supplement each other, and it is worth while to look at how they both work.

The Macroscopic Approach

Before much was known about atoms and their behavior, only the macroscopic approach was available. This way of thinking, sometimes called the *phenomenological* way, does not inquire into the ultimate construction of a solid. It reaches its conclusions without needing to know that construction.

The thinking shows, for example, that any solid bit of matter must necessarily contract, much or little, when pressure is applied to it. Steel, wood, glass—all must obey that rule. You may say, "Of course. What else would you expect?" But before you brand the rule trivial, examine another example. Solids usually contract when they are cooled. Must all solids contract when cooled, as they must when pressed? No, some expand.

When no phenomenological rule asserts that a usual sort of behavior is a necessary sort of behavior, we can expect to find exceptions to the rule. Nature is so diverse that she can provide exceptions to any but the rigorous rule. But the macroscopic approach, from which a solid appears to be a structureless piece of matter, can do little to help in finding the exceptions and nothing to explain them.

The little that it can do, however, cannot be neglected. If a solid exhibits one sort of exceptional behavior, then that behavior may imply that the solid is necessarily exceptional in some other way as well. In other words, there may again be a phenomenological rule asserting that *if* so-and-so is true, *then* such-and-such must be the case.

For example, most liquids contract when they freeze. But everyone whose plumbing has burst in cold weather knows that water is exceptional. Ice takes up more space than the water from which it was formed and floats on water for that reason. Conversely, although it is less obvious, pressure makes ice melt at a temperature lower than its usual melting point. These two kinds of behavior have a necessary connection; either implies the other.

Thus, the familiar observation that ice floats on water enables us to predict the unexpected fact that ice under pressure will melt at a lower temperature. The ice skater glides on a thin film of water produced by the weight of his body, and the water freezes again when he has passed.

This behavior exemplifies a particular class of the properties of matter that can be approached with great success macroscopically. Those properties are called *reversible*. To see how reversible properties are distinguished from other kinds, look at how some familiar mechanical properties of solids might be classified.

Reversibility, Transport, and Catastrophe

When a solid object is pulled in opposite directions on opposite ends, when it is squeezed, twisted, or bent, a *stress* is applied to it. The solid responds to the stress by acquiring a *strain,* a change in its size or shape. A uniform pressure is a special kind of stress, and the resulting decrease of volume is a special kind of strain.

If the stress is sufficiently small, removing the stress will remove the strain—the solid will spring back to its original shape. In short, this *elastic* behavior of solids is reversible, and the elasticity of solids is a reversible property.

A larger stress may exceed the *elastic limit* of the solid so that when the stress is removed, the solid springs only part of the way back. The permanent change of shape is a consequence of the *plastic flow* of the material. A still larger stress will make a *cata-*

strophic change in the solid—the piece will break apart. Flow and fracture are *irreversible* properties—the effects remain after their causes have disappeared.

It is interesting to classify some of the electrical properties of solids in an analogous way. If two pieces of metal are placed on opposite sides of a thin sheet of mica and then connected by wires with the terminals of a battery, the mica will not conduct an electric current continuously. But as soon as the pieces of metal are connected with the battery, a pulse of current will *polarize* the mica electrically—or charge it, to use the popular word. If the wires are then disconnected from the battery and touched together, there will be a pulse of current through them in the opposite direction, discharging the mica.

Discussing this phenomenon a hundred years ago, James Clerk Maxwell wrote,

> Here, then, we perceive another effect of electromotive force, namely, electric displacement, which according to our theory is a kind of elastic yielding to the action of the force, similar to that which takes place in structures and machines owing to the want of perfect rigidity of the connexions.*

Such *dielectric* polarization occurs also in all electrical insulators; it is a reversible electrical property analogous to their mechanical elasticity.

A stronger battery may drive a continuous trickle of electric current through an insulator, especially if the insulator is hot. In other words, a high enough voltage slowly pushes electric charges through the solid, somewhat as a high enough stress slowly transports some of the material into a new position. Finally, a very high voltage will drive a spark through the solid, leaving a little trail of catastrophe behind it.

Some thermal properties of solids can be classified in similar terms. When a hot object is put in contact with a cold object, heat flows from the hot object into the cold object until their temperatures are the same. If the newly heated object is then put in contact with another cold object, the heat will flow out of it again. Each

**Philosophical Transactions of the Royal Society* (London), Series A, CLV (1865), 459.

object has a capacity for absorbing heat, and under suitable circumstances it will return the heat that it absorbs. You can think of a difference of temperature as somewhat like a force that drives heat. Heat capacity thus stands out as a reversible property and heat conduction as a *transport* property.

Heated to a high enough temperature, a solid object may melt, absorbing quite a lot of heat as it does so. If the molten material is cooled, it will solidify again and return the heat. From that point of view, fusion is a reversible process. But from another point of view it is catastrophic, for the solid stops being solid when it melts and must be made anew. This second point of view is shown in Table 1, which summarizes the preceding classification.

TABLE 1. A Suggested Classification of Some Properties of Solids

	Reversible	Transport	Catastrophic
Mechanical	Elastic distortion	Plastic distortion	Rupture
Thermal	Heat capacity	Heat conduction	Melting
Electrical	Dielectric polarization	Electrical conduction	Dielectric breakdown

Both the macroscopic and atomistic approaches treat the reversible properties of solids more successfully than the irreversible properties. The theory of elasticity is a good example of the macroscopic study of a single reversible property. In that theory, mathematical methods are employed to deduce many consequences of two simple observations.

The first, sometimes called *Hooke's law*, is the fact that the strain in a solid is proportional to the stress producing it, so long as the solid is not stressed beyond its elastic limit. The second observation is the fact that the mechanical work done on a solid, by stressing it below its elastic limit, can be completely recaptured as mechanical work when the stress is removed. The deduced behavior of solid objects under static loads and in vibration is a cornerstone of much modern mechanical engineering.

Couplings and Their Converses

But applying stresses is not the only way of producing strains. The mechanical, thermal, and electrical properties of a solid do not live in isolation from one another. The expansion of a solid when it is heated is an instance of a thermal influence producing a mechanical effect: a change of temperature produces a strain. There are similar couplings between all these properties, and they are especially interesting when the properties coupled are reversible.

About two hundred years ago Franz Aepinus noticed that when the gem stone tourmaline is heated, it becomes electrified. Later work showed that a change of temperature polarizes tourmaline electrically in much the same way that an electric battery polarizes mica. In tourmaline and in many other crystals—even crystals of ordinary sugar—a thermal influence produces an electrical effect called the *pyroelectric effect.*

In 1880 the brothers Pierre and Jacques Curie discovered that many crystals exhibit another curious coupling between their reversible properties. Quartz and Rochelle salt crystals are instances of materials that can be electrically polarized by a mechanical stress. This *piezoelectric effect* has had wide application—in phonographs, for example—for translating mechanical motions into electrical impulses. Thus, the circle of couplings (Fig. 1) between

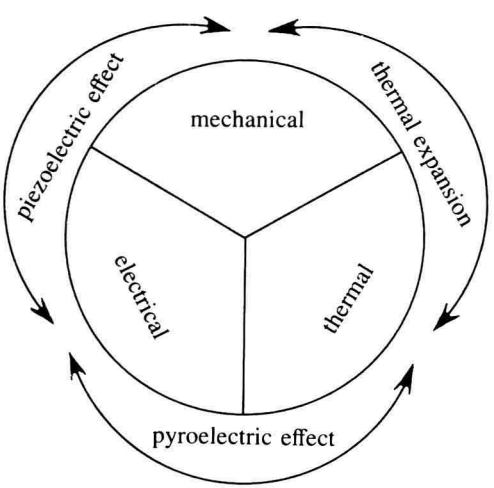

FIG. 1—Couplings between the reversible properties of a solid.

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the reversible mechanical, thermal, and electrical properties of solids has been closed by instances of the three possible types.

You may feel that the circle is not quite closed until you have found solids that behave conversely—instances in which an electrical influence produces a mechanical or a thermal effect. But here the macroscopic theory provides the answer that you have found such instances already. This is typical of the answers that the theory can give regarding couplings between reversible properties.

If, for example, a solid exhibits the piezoelectric effect—in which a mechanical influence produces an electrical result reversibly—then that same solid will exhibit the converse effect—that is, an electrical influence will produce a mechanical result. A voltage applied to the crystal will change its shape slightly; when the voltage is removed, the crystal will return to its original shape. Indeed, if you measure the magnitude of either of these effects, you need not measure the other. You can calculate either from its converse by using the macroscopic theory, without recourse to an atomistic approach.

The Conservatism of Matter

Even without calculation we can get some useful qualitative ideas of how the macroscopic theory connects the reversible coupling properties of matter. One connection can be made by a powerful generalization, often called the *principle of mobile equilibrium,* stated by Henri Le Châtelier in 1884 and sometimes called the *Le Châtelier principle.*

This principle says that matter resists change: when it is forced to change, it opposes the force with all the means at its disposal. You can see most clearly how to use the principle by recalling the behavior of a gas under pressure.

When a gas is compressed, it is forced to occupy a smaller volume. It must comply, but it complies as reluctantly as it can. A rise in its temperature would tend to make its volume increase and so help oppose the force. Therefore, as anyone who operates a tire pump will notice, compressing a gas raises its temperature.

Similarly, the Le Châtelier principle connects the properties of ice discussed above. Imagine a mixture of ice and water just at the freezing temperature, so that none of the ice is melting and none of

the water is freezing. Pressure exerted on the mixture forces it to occupy a smaller volume. Since water occupies a smaller volume than ice, some of the ice is forced to melt into water, so that the volume is reduced. At the same time the temperature will go down, in an effort to keep the ice frozen and prevent the decrease in volume. Here is a case that behaves opposite to the gas in a tire pump; pressure reduces the temperature instead of raising it.

You may be interested in performing two experiments on two analogous properties of an ordinary rubber band. For the first experiment, hold the ends of the band in both hands and stretch it to four or five times its normal length. Keep it stretched for a minute or so—long enough to insure that its temperature is the same as that of the room—then let it retract to its normal length. Now quickly touch the tip of your tongue, a sensitive thermometer, to the rubber band. Is it hotter or colder than you would expect? If you are in doubt, compare it with a similar rubber band that you have not stretched.

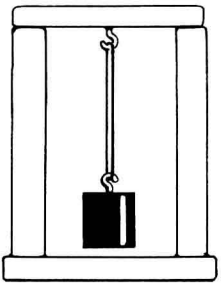

FIG. 2—A rubber band stretched by a weight.

For the second experiment, arrange a weight so that it hangs freely from the rubber band (Fig. 2). Measure the length to which the weight stretches the band, and then put the whole assembly in the refrigerator. After giving the band a few minutes to cool, measure its length again while it is still cool and compare the new length with the previous length. By the Le Châtelier principle, you can connect these observations of length with the observations of temperature in the first experiment.

The Atomistic Approach

Note, however, that reasoning of this kind cannot predict the

magnitudes of the effects that you observe. It can only connect the two facts that the rubber band is cooler when you have finished your first experiment and that it becomes longer in the refrigerator in your second experiment. And the results of the theory of elasticity can contain only algebraic symbols for the constants of proportionality between stress and strain. The only way to substitute a number for a symbol is to measure the ratio of the strain to the stress in a sample of a material in question. Taken alone, the theory lacks names and numbers.

An ideal of the second approach to solids—the *microscopic,* or *atomistic,* approach—is to add those names and numbers—to penetrate more deeply into the behavior of solids and to deduce their observed properties from a knowledge of the way they are constructed by their constituent atoms and from a knowledge of the physical behavior of those atoms. The history of this approach extends back more than a hundred years. Indeed, an atomic constitution of matter had been suspected for two millenia. But the accomplishments of the atomistic approach were meager until, in this century, the discovery of X-ray diffraction by crystals and the invention of wave mechanics opened avenues for systematic progress.

The idea that all forms of matter are made of atoms provides at once a picture of the differences among the three states of matter—gaseous, liquid, and solid. In gases the atoms (or perhaps the molecules, each consisting of a few atoms tightly tied together) are flying about as tiny, self-sufficient units. They move quite independently and influence one another very little, except during the instants when two collide and one picks up speed at the expense of the other. If the gas were not confined in a container, the molecules would fly off in all directions.

When the temperature of the gas is reduced, the average speeds of the molecules are reduced also, and the molecules have a chance to respond to the attractive forces they exert on one another. At a low enough temperature, those forces will bring them together to form a liquid. The molecules are packed quite tightly in a liquid, but they are still moving. In particular, they can move past one another and permit the liquid to flow.

At an even lower temperature, the liquid solidifies. In the solid

the molecules are packed only very little more tightly than in the liquid (indeed, in ice they are packed *less* tightly), but they can no longer move past one another easily. Their motion is a vibration about fixed positions from which they do not stray far. Even at a temperature of absolute zero, were it attainable, the molecules would continue to vibrate a little, with the so-called *zero-point vibrations*.

In the picture of solids as built of molecules tightly packed together in mutual attraction and subject to constant thermal agitation, it is clear why a quantitative atomistic theory of solids is difficult to perfect. When constructed from first principles, mathematical equations describing the behavior of a collection of particles as unimaginably numerous as the atoms in a solid become too complicated to solve and too opaque to give insight. Characteristically, the physics of solids retreats from the ideal of deducing the exact quantitative behavior of solids from first principles and sets itself a more modest goal.

The Atomistic Goal

That goal is insight rather than exact calculation. In pursuing it, the physicist first separates out a particular phenomenon for study and makes an educated guess at what atomic behavior is largely responsible. He then sets up an imaginary model which embodies that behavior and neglects all the confusing details he thinks may be unimportant. He calculates how the model will behave and compares his answer with the results of experiments on actual solids. If his result is in rough agreement with experiment, he accepts his model as a correct explanation of the phenomenon, that is, a simplified approximation of it.

Clearly, several factors must conspire to make this effort successful. In his educated guess, the physicist tentatively builds an additional insight on the past insights of others, with which he has had to make himself acquainted. His model must be consistent with other successful models used in discussing other phenomena, for although the phenomena may be different, the solid in which they are occurring is the same. In constructing the model, the physicist must be adroit enough to make it mathematically manageable, so that he can get a numerical answer for the crucial comparison with experiment. And he must use good physical sense in deciding what

degree of agreement with experiment is *good* agreement; in some cases good agreement may mean within 10 percent, in others within a factor of 10.

Throughout most of this book you will see the atomistic method at work. And you will notice that the models are built with no more detail than needed to describe the behavior they were invented to explain. This habitual economy obeys a deep-lying aesthetic principle of all the sciences, often called "Occam's razor": Let not hypotheses be multiplied beyond those necessary to explain the facts. A physicist will try to remove from a model those details which are irrelevant to his purpose. And he will try to avoid using an atomistic model for a purpose that could have been served as well without the assumption that matter is composed of atoms, that is, by a macroscopic argument.

The earliest and simplest atomistic models of a solid—those devised for explaining heat capacity—are discussed in the next two chapters. Their simplicity and success have combined to put them in an especially important position among solid models.

II. HEAT

It is odd to think that there is a word for something which strictly speaking does not exist, namely, rest.
MAX BORN, *The Restless Universe*

DURING the nineteenth century, physicists succeeded in their quest for precise ideas about the two major thermal quantities—heat and temperature. In earlier days it had seemed natural to suppose that the heat which flowed from a hot to a cold body was some unique substance. But about the year 1800 many experiments, especially those of Count Rumford, showed that the heat in hot bodies is associated with a mode of *motion*—a disorganized random motion of their constituent molecules.

Thus, the heating of a cold body is now visualized as an excitation of the motion of its molecules by the impacts of the molecules in the hot body. Both the heat that flows and the temperature differences that urge it to flow can be related to those molecular motions.

The Energy of Heat

Even before 1800 many measurements had been made of the amount of heat required to change the temperatures of various substances by various amounts, and *heat capacity*—the amount of heat necessary to raise the temperature of a given mass of the substance by one degree—had been tabulated. In trying to bring order to these data, Pierre Dulong and Alexis Petit made an important observation shortly after Count Rumford's death. They noticed that most of the chemical elements in solid form absorbed nearly the same amount of heat, regardless of the species of the

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