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Cambridge University Press
978-0-521-65151-6 - Structure of Materials: An Introduction to Crystallography, Diffraction, and Symmetry
Marc De Graef and Michael E. McHenry
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CHAPTER

1 Materials and materials properties

> *"We proceed to distribute the figures [solids] we have described between fire, earth, water, and air . . . Let us assign the cube to earth, for it is the most immobile of the four bodies and most retentive of shape; the least mobile of the remaining figures (icosahedron) to water; the most mobile (tetrahedron) to fire; the intermediate (octahedron) to air. There still remained a fifth construction (dodecahedron), which the god used for embroidering the constellations on the whole heaven."*
>
> Plato, *Timaeus*, 427–347 BC

1.1 Materials and structure

The practice of using organic and inorganic materials is many millennia old. Oxide pigments were used in early cave paintings, flint tools were used in the *Stone Age* and precious metal smelting was prevalent in the Nile Valley as early as 5000 years ago (Klein and Hurlbut, 1985). Extractive metallurgy led to the use of metals in the *Bronze Age* and *Iron Age*. The extraordinary advances made possible by electronic materials have led some to suggest that we are in the midst of the *Silicon Age*. It is clear that the prior materials ages evolved slowly through the accumulation of empirical knowledge. The present materials age is evolving at a more rapid pace through the development of synthesis, structure, properties and performance relationships, the *materials paradigm*.

In this book, we will introduce many concepts, some of them rather abstract, that are used to describe solids. Since most materials are ultimately used in some kind of application, it seems logical to investigate the link between the atomic structure of a solid, and the resulting macroscopic properties. After all, that is what the materials scientist or engineer is really interested in: how can we make a material useful for a certain task? What type of material do we need for a given application? And why can some materials not be used for particular applications? All these questions must be answered when a material is considered as part of a design. The main focus of the book is on the fundamental description of the positions and types of the atoms, the ultimate building blocks of solids, and on the experimental techniques used to determine how these atoms are arranged.

We now know that many of the materials we use every day are *crystalline*. The concept of crystalline solids and the development of experimental techniques to characterize crystals are recent developments, although certain kernels of thought on the basic building blocks of solids can be traced to much earlier times. For example, the quote beginning this chapter is attributed to the Greek philosopher Plato (427–348/347 BC); in his dialogue *Timaeus*, he discussed his theory of the structure of matter. He postulated that the basic particles of earth, air, fire, and water had the form of the regular *Platonic solids* (Fig. 1.1). Plato believed that it was possible to group these basic particles into crystal shapes that filled space. In our current understanding of the structure of solids, the shapes that are combined to fill space are known as *unit cells*, and we distinguish seven major shapes, more formally known as the seven *crystal systems*.

For crystalline solids we will define a standardized way to describe crystal structures. We will also describe experimental methods to determine where the atoms are in a given crystal structure. We will rely on mathematical techniques to develop a clear and unambiguous description of crystal structures, including rules and tools to perform crystallographic computations (e.g., what is the distance between two atoms, or the bond angle between two bonds, etc.). We will introduce the concept of *symmetry*, a unifying theme that will allow us to create classifications for crystal structures.

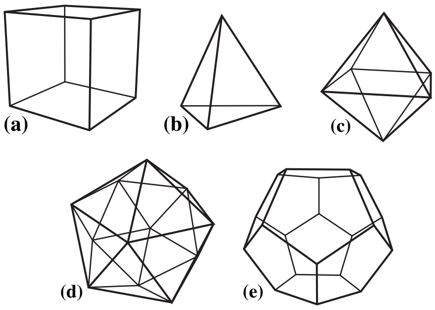

Fig. 1.1. The five Platonic solids: (a) cube, (b) tetrahedron, (c) octahedron, (d) icosahedron, and (e) pentagonal dodecahedron.

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1.2 Organization of the book

The first half of the book, Chapters 1 through 13, deals with the basics of crystallography. It covers those aspects of crystallography that are mostly independent of any actual material, although we will frequently use actual materials as examples to clarify certain concepts and as illustrations. The second half of the book, Chapters 15 through 25, looks at the structure of broad classes of materials. In these chapters, we consider metals, oxides, and molecular solids. This subject matter helps the reader build an understanding of atomic structures, from simple to complex. Where possible, we also illustrate technologically important materials. In these later chapters, we will introduce many geometrical principles that can be used to understand the structure of materials. Such principles enrich the material presented in Chapters 1 through 13, and allow us to gain insight into the structure of quasicrystalline and amorphous materials discussed in advanced chapters in the second half of the text.

Chapter 14 forms the connection between the two halves of the book: it illustrates how techniques of the first half are used to study the structures of the second half. We will discuss this connection by means of four different materials, which will be introduced later in this first chapter. Some topics are more advanced than others, and we have indicated these sections with an asterisk at the start of the section title. Each chapter has an extensive problem set, dealing with the concepts introduced in that chapter. At the end of each chapter, we have included a short historical note, highlighting how a given topic evolved, listing who did what in a particular subfield of crystallography, or giving biographical information on important crystallographers.

In the later chapters, we give examples of crystallographic computations that make use of the material presented in the earlier chapters. We illustrate the relationship between structures and phases of matter, allowing us to make elementary contact with the concept of a *phase diagram*. Phase relations and phase diagrams combine knowledge of structures and thermodynamics.[1] Prominent among the tools of a materials scientist are those that allow examination of structures on a nanoscale. Chapters in the latter half of the book will have further illustrations of interesting nanostructures.

We begin, in this chapter, with a short discussion of length scales in materials. Then we introduce the concepts of *homogeneity* and *heterogeneity*. We will talk about material properties and propose a general definition for a material property. We continue with a discussion of the directional dependence of certain properties and introduce the concepts of *isotropy* and *symmetry*. We conclude the chapter with a preview of some of the things this book has to offer.

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[1] In a materials science or materials engineering curriculum, phase relations and diagrams are typically the subject of the course following a structures course.

1.3 About length scales

When we talk about crystals, most of us will think about the beautiful crystalline shapes that can be found in nature. Quartz crystals are ubiquitous, and we can recognize them by their shape and color. Many naturally occurring crystals have sizes in the range from a few millimeters to a few centimeters. These are objects that we can typically hold in our hands. When it comes to describing the structure of a crystal at the atomic level, we must reduce the length of our measuring stick by many orders of magnitude, so it might be useful to take a brief look at the relevant length scale. In addition, when we wish to study, say, the distance between a pair of atoms, we must use an experimental measuring stick that is capable of measuring such tiny distances. The human eye is obviously not capable of "seeing atoms," but there are several alternative observation methods that *are* capable of operating at the atomic length scale.

The size of an atom is of the order of 10^{-10} meters. This particular distance is known as the Ångström, i.e., $1\,\text{Å} \equiv 10^{-10}\,\text{m}$. It is convenient to stick to the so-called *metric system*, and the closest standard metric unit is the *length unit, nanometer* (nm), which is defined as $1\,\text{nm} \equiv 10^{-9}\,\text{m}$, so that $1\,\text{Å} = 0.1\,\text{nm}$. In this book, we will use the nanometer as the standard unit of length, so that we can express all other distances in terms of this unit. For instance, 1 micrometer (μm) equals 10^3 nm, and one millimeter (mm) is equal to 10^6 nm. An illustration of the range of object sizes from the atomistic to the "human" length scale is shown in Fig. 1.2.[2] The central vertical axis represents the size range on a logarithmic scale; going up one tick mark means a factor of 10 larger. To the right of the figure, there are a few examples of objects for each size range. In the scientific community, we distinguish between a few standard size ranges:

- *macroscopic*: objects that can be seen by the unaided eye belong to the class of the macroscopic objects. An example is the quartz crystal shown in the top circle to the right of Fig. 1.2.
- *microscopic*: objects that can be observed by means of optical microscopy. The second circle from the top in Fig. 1.2 shows individual grains in a $\mathrm{SrTiO_3}$ polycrystalline material. The lines represent the boundaries between grains, the darker spots are pores in the ceramic material.
- *nanoscale*: objects with sizes between 1 nm and 100 nm. The third circle shows a set of nano-size particles of a MnZn ferrite with composition $\mathrm{Mn_{0.5}Zn_{0.5}Fe_2O_4}$.

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[2] With "human length scale" we mean objects that can be found in our societies: chairs, houses, vehicles, and so on, i.e., objects with sizes typically less than 10^2 m or 10^{11} nm. In this book, we will have no need for larger sizes.

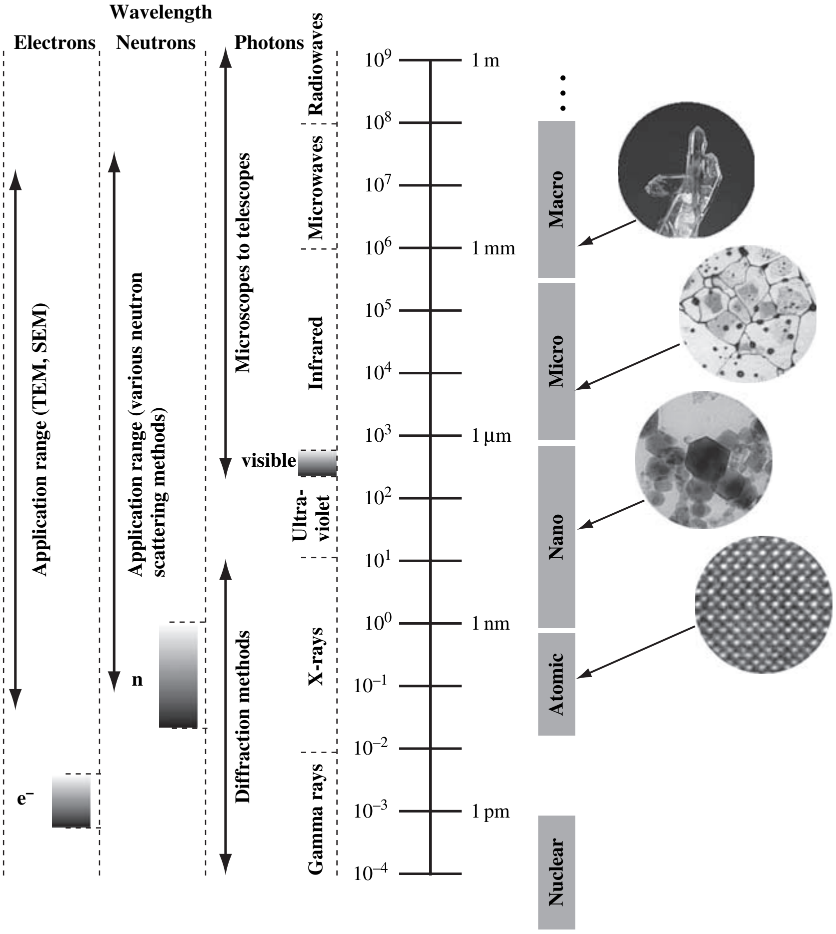

Fig. 1.2. Schematic illustration of the various length scales, from macroscopic, to microscopic, to nanoscale, to the subatomic. The left hand side of the figure shows the experimental techniques that are used to cover the various length scales. The images in the circles on the right are (from the top down): a quartz crystal (courtesy of D. Wilson); grains in a $SrTiO_3$ ceramic (courtesy of G. Rohrer); nano-crystalline particles of $Mn_{0.5}Zn_{0.5}Fe_2O_4$ (courtesy of R. Swaminathan); atomic resolution image of $BaTiO_3$.

- *atomistic*: the bright dots in this image correspond to the Ba and Ti ions in a tetragonal $BaTiO_3$ crystallite. This is a so-called high resolution image, obtained by transmission electron microscopy, where one can distinguish individual columns of atoms with a distance between the atoms of around 0.2 nm.

The ability to observe an object of a certain size is closely linked to the *wave length* of the radiation used for the observation. Consider circular waves that travel on a large pond after you toss a rock into the water. If an object, much smaller than the distance between the crests of the waves (the *wave length*), floats on the water nearby, then the waves will pass by the object without being perturbed by the object; the object will move up and down with the passing waves. If the object is large compared to the wave length, say, a concrete pillar or a wall, then the waves will be perturbed, since they have to travel around the object; often, part of the waves will be reflected by the object. If waves are not perturbed by an object, then this object is essentially *invisible* to those waves. If we use visible light, with a wave length of around 500 nm, to look at viruses (with a typical size between 3 and 300 nm), then the light waves will not be perturbed significantly by the viruses, and, therefore, we will not be able to observe viruses using optical microscopy methods.

To determine the smallest thing the human eye can see, we must understand the structure of the eye. The human eye is a sphere with an approximate diameter of 25 mm. It has a lens with an opening (pupil) of about 3.5 mm. The inside back surface of the eye is covered with two types of light receptors: rods and cones. The cones are concentrated in a small area, 0.3 mm diameter, directly opposite the lens. This area is known as the *fovea*. There are about 15 000 cones in the fovea, leading to a cone density of about 200 000 per mm^2. Each cone is about 1.5 μm in diameter, and the average spacing between cones is 2.5 μm. For convenience, we can imagine the cones to be packed in a hexagonal array, as shown by the small gray disks in Fig. 1.3.

If we consider an object at a distance of 250 mm from the eye, then this object will be imaged by the lens onto the fovea with a magnification factor of $M = 0.068$ (Walker, 1995). Consider a set of narrowly spaced lines, with a line density of ρ lines per millimeter (lpm). The eye lens will image this grid of lines onto the fovea, so that the line density at the fovea becomes $\rho_\mathrm{f} = \rho/M$ (since the eye demagnifies the object size, the line density will become larger). The highest line density that can be "seen" by the fovea corresponds to each line being projected onto a row of cones, and the next row does not have a line projected on it. Since the average spacing of the cones is 2.5 μm, the smallest possible distance at which the lines can still be resolved by individual rows of cones is $2.5\sqrt{3} = 4.3$ μm. A line spacing of 4.3 μm leads to a line density at the fovea of $\rho_\mathrm{f} = 230$ lpm, which corresponds to a line density at the object of 15.6 lpm. So, at a distance of 250 mm, the human eye, in the best possible conditions, can see the individual lines in a grid with about 16 lines per mm.

The discussion in the preceding paragraph describes an idealized case; in reality, the highest resolvable line density at a distance of 250 mm

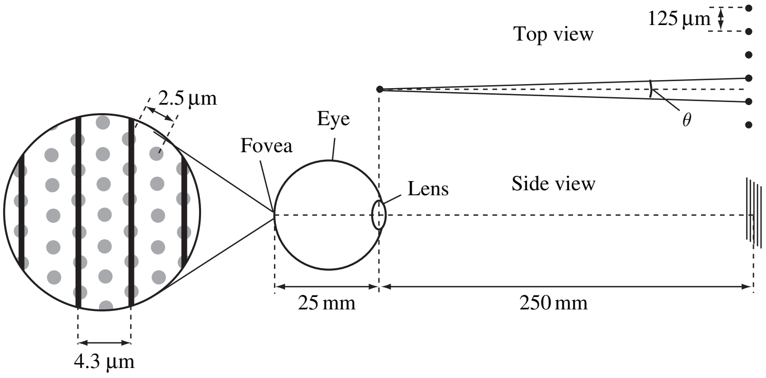

Fig. 1.3. Schematic illustration of the resolution of the human eye. The lower portion shows the fovea as a hexagonal array of cones, the top view shows the angular resolution of the eye in terms of the eye–object distance, the angle θ, and the distance between individual object lines.

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is about 8 lpm. It is more convenient to express these numbers in terms of the angle between two lines leaving the eye and reaching two neighboring lines of the grid, as shown in the top view of Fig. 1.3. Simple trigonometry shows that $\theta = 0.125/250$, so that $\theta = 5\times10^{-4}$ radians, or 0.029°, which is equivalent to 1.7 arc minutes. Rounding up, we can say that the human eye has a visual resolution limit of 2 arc minutes per line pair. Similar numbers are obtained when the object consists of dots or other shapes. It should be clear to the reader that the human eye is not capable of resolving microscopic objects, let alone the distance between atoms.[3]

Returning to Fig. 1.2, the columns on the left hand side of the figure indicate the range of applicability of a number of important materials characterization methods. Each method relies on the use of a particular type of particle: electrons, neutrons, and photons (or electromagnetic radiation). All three of these methods are capable of producing information about the atomic structure of matter. In this book, we will discuss mostly the use of X-rays for structure determination, but we will also describe briefly how neutrons and electrons can be used to obtain similar information.

1.4 Wave–particle duality and the de Broglie relationship

By the early part of the 20th century it had been established that electromagnetic (EM) radiation (light) has both a wave and particle (photon) character, the *wave–particle duality*. James Clerk Maxwell proposed a *theory of electromagnetism* (Maxwell's equations) which put the wave nature of light on a formal mathematical basis by the late nineteenth century. However, the *photoelectric effect* was explainable only in terms of the particle aspects of light (Albert Einstein, 1905). Einstein's formula relates the energy of a photon, E, to the frequency of radiation, ν:

$$\boxed{E = \mathrm{h}\nu,} \tag{1.1}$$

The wave length of electromagnetic radiation is related to the frequency, ν, of the wave (the number of cycles per second) by means of the following relation:

$$\boxed{\lambda = \frac{\mathrm{c}}{\nu},} \tag{1.2}$$

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[3] It is noteworthy that the human eye, as compared to a digital camera, has a remarkably high pixel density. While the cone and rod densities vary across the eye, on average, the eye corresponds to a 600 megapixel camera for a 120° field of view! Of course, the eye produces a continuous stream of images, more like a movie than a still image. Nevertheless, the amount of information processed by the eye and brain is truly remarkable.

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where $c = 299\,792\,458\,\mathrm{m/s}$ is the velocity of light in vacuum. A consequence of Einstein's explanation of the photoelectric effect was that EM waves could be thought of as having particle-like momentum.

The wave length, λ, of electromagnetic radiation spans many orders of magnitude, from the long wave length radio waves (see Fig. 1.2) to visible light to X-rays and gamma rays. Visible light cannot be used to observe the atomistic length scale, but X-rays have a wave length that is comparable to the distance between atoms. Hence, X-ray waves will be perturbed by atoms, and we can make good use of this perturbation, as we will see in later chapters.

Similar relations can be derived for electrons and neutrons. Louis de Broglie, using formulae from Einstein's special theory of relativity, argued that if electromagnetic waves also have a particle nature, should not particles such as the electron also have a wave nature? For a particle with mass, m, moving with velocity v, he proposed an associated wave characterized by the wave length:

$$\lambda = \frac{\mathrm{h}}{mv}\ . \tag{1.3}$$

For electrons accelerated by a voltage, V, the electron wave length is given by:

$$\lambda = \frac{\mathrm{h}}{\sqrt{2m_0 eV}}, \tag{1.4}$$

where $\mathrm{h} = 6.626\,075 \times 10^{-34}\,\mathrm{J\,s}$ is Plank's constant, $e = 1.602\,177 \times 10^{-19}\,\mathrm{C}$ is the electron charge, and $m_0 = 9.109\,389 \times 10^{-31}\,\mathrm{kg}$ is the rest mass of the electron. In 1927, Davisson and Germer showed experimentally that electrons do indeed have wave character by causing them to undergo diffraction like X-rays, through a crystal lattice (Davisson and Germer, 1927a). This experiment laid the basis for measuring crystal structures by the method of low energy electron diffraction (LEED), and, later on, for the invention of the transmission electron microscope.

In the case of high energy electrons where the accelerating voltage, V, is large, a relativistic correction is made and the electron wave length is given by:

$$\lambda = \frac{\mathrm{h}}{\sqrt{2m_0 eV(1 + \frac{e}{2m_0\mathrm{c}^2}V)}}. \tag{1.5}$$

Table 1.1 lists a few representative electron wave lengths used in scanning and transmission electron microscopes.

The wave length of neutrons also follows from the de Broglie relation:

$$\lambda = \frac{\mathrm{h}}{m_n v}, \tag{1.6}$$

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Table 1.1. Electron wave lengths (in pm) for selected acceleration voltages *V* for scanning electron microscopes (left two columns) and transmission electron microscopes (right two columns).

V (Volt)	λ (pm)	V (Volt)	λ (pm)
1 000	38.76	100 000	3.701
5 000	17.30	200 000	2.508
10 000	12.20	300 000	1.969
20 000	8.59	400 000	1.644
		1 000 000	0.872

where $m_n = 1.674\,929 \times 10^{-27}$ kg is the neutron rest mass and v is its velocity. However, neutrons are not charged particles and, therefore, they are not accelerated by a voltage. Neutrons are created in nuclear fission processes inside nuclear reactors, as described in more detail in Chapter 13. Typically, a wide range of neutron velocities emerges from the reactor, and by selecting only neutrons within a certain narrow velocity window, one can select a particular wave length. For instance, to obtain a neutron with a wave length of 0.1 nm, one would have to select a velocity window at $v = 3.96 \times 10^3$ m/s, or approximately 4 km/s. It is also possible to have neutrons reach thermal equilibrium, so that their kinetic energy is:

$$E_{\text{kin}} = \frac{1}{2} m_n v^2 = \frac{3}{2} \mathrm{k_B} T, \tag{1.7}$$

where $\mathrm{k_B} = 1.38 \times 10^{-23}$ J/molecule/K is the Boltzmann constant. The de Broglie relation then becomes:

$$\lambda = \frac{\mathrm{h}}{\sqrt{3 m_n \mathrm{k_B} T}}. \tag{1.8}$$

1.5 What is a material property?

1.5.1 Definition of a material property

We choose materials to perform well in certain applications. For instance, we use steel beams and cables in bridges, because they provide the strength and load-bearing capacity needed. We use plastics in toys because they can be molded into virtually any shape and they are strong and light weight. When we use a material in a certain application, we know that it will be subjected to particular external conditions, e.g., a constant load, or a high temperature, or perhaps an electrical current running through the material. In all these cases, we must make sure that the material responds in the desired way. For a bridge deck held up by steel cables, we want the cables to retain their strength

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all year round, regardless of the weather and temperature, and regardless of the number of cars and trucks crossing the bridge. For a computer chip, we want the semiconductor material to behave predictably for the lifetime of the computer.

In general, we want a material to have a particular response to a given external influence. This basic statement can be cast in more formal, mathematical terms. We will represent the external influence by the symbol $\mathcal{F}$, which stands for *Field*. This could be an electrical or magnetic field, a temperature field, the earth's gravitational field, etc. The material will respond to this field, and the *Response* is described by the symbol $\mathcal{R}$. For instance, the response of a steel beam to an external load (i.e., a weight at the end of the beam) will be a deflection of the beam. The response of a conductor to an electrical field applied between its two ends will be an electrical current running through the conductor. In the most general sense, the relation between field and response is described by:

$$\mathcal{R} = \mathcal{R}(\mathcal{F}), \tag{1.9}$$

i.e., the material response is a function of the externally applied field. It is one of the tasks of a materials scientist to figure out what that function looks like.

Once we recognize that the behavior of a material under certain external conditions can be expressed in mathematical terms, we can employ mathematical tools to further describe and analyze the response of this material. We know from calculus that, for "well-behaved" functions, we can always expand the function into powers of its argument, i.e., construct a Taylor expansion.[4] For equation 1.9 above, the Taylor expansion around $\mathcal{F} = 0$ is given by:

$$\mathcal{R} = \mathcal{R}_0 + \frac{1}{1!}\left.\frac{\partial\mathcal{R}}{\partial\mathcal{F}}\right|_{\mathcal{F}=0}\mathcal{F} + \frac{1}{2!}\left.\frac{\partial^2\mathcal{R}}{\partial\mathcal{F}^2}\right|_{\mathcal{F}=0}\mathcal{F}^2 + \frac{1}{3!}\left.\frac{\partial^3\mathcal{R}}{\partial\mathcal{F}^3}\right|_{\mathcal{F}=0}\mathcal{F}^3 + \ldots \tag{1.10}$$

where $\mathcal{R}_0$ describes the "state" of the material at zero field. There are two possibilities for $\mathcal{R}_0$:

(i) $\mathcal{R}_0 = 0$: in the absence of an external field ($\mathcal{F} = 0$), there is no permanent (or remanent) material response. For example, if the external field is an applied stress, and the material response is a strain, then at zero stress there is no strain (assuming linear elasticity).

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[4] Recall that a Taylor expansion of a function $f(x)$ around $x = 0$ is given by

$$f(x) = f(0) + \sum_{n=1}^{\infty}\frac{1}{n!}\left.\frac{\mathrm{d}^n f}{\mathrm{d}x^n}\right|_{x=0} x^n$$

where $n! = 1 \times 2 \times 3 \times \ldots \times (n-1) \times n$ is the factorial of n. If the function f depends on other variables in addition to x, then the derivatives $\mathrm{d}^n/\mathrm{d}x^n$ must be replaced by partial derivatives $\partial^n/\partial x^n$.