

# Atoms and Aggregates of Atoms

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## 1 Introduction

The physical behavior of a given material may be characterized by a set of *macroscopic*, measurable quantities, such as the electrical conductivity of the material, its coefficient of expansion, its magnetic permeability, its dielectric constant, etc. In general, these quantities are functions of externally variable parameters, such as temperature, pressure, frequency of the applied field, etc. The functional relationships between the characteristic quantities and the variable parameters can be established from experimental results, and constitute an important part of our technical and scientific knowledge. In this book we shall be concerned with problems which arise when one asks why a certain functional relationship between a characteristic quantity and a parameter exists. We shall try to answer such a question in terms of the properties of the atoms which constitute the material; i.e. we shall accept the idea that materials consist of atoms, and that atoms consist of nuclei and electrons, and shall attempt to derive the observed relationships in terms of our knowledge of atoms. Actually we shall, in most cases, assume a much simpler "model" for the atomic constituents than is justified in terms of our present-day knowledge of atoms. The reason for this is that in most cases the calculations involved in arriving at a certain relationship would be too complicated if they were attempted on the basis of first principles. For example, it is impossible to calculate exactly the dielectric constant of a material. On the other hand, we can learn a great deal about the behavior of dielectrics if we are willing to accept certain simplifications concerning the structure and properties

of the atoms. Simplified atomic models will thus play an important role in the discussions in this book. The reader should always realize that the results of calculations pertaining to such models cannot be expected to provide exact numbers. The main purpose of the model is that it can provide the correct functional relationship between certain quantities, and thereby provide insight into the essential mechanism which determines such a relationship. On the basis of this understanding predictions can frequently be made concerning the properties of a large group of materials. In other words, the atomic models unify our understanding of the properties of materials and as such prove their scientific usefulness.

In this book we shall discuss only a limited number of properties. In particular we shall be concerned with the dielectric and magnetic properties of materials used in electrical engineering, and with the mechanism of electrical conductivity. The materials under discussion are in most cases crystalline solid materials. It is desirable to realize from the beginning that the properties of solids are not simply given by the sum total of the properties of the atoms which make the solid. In fact, a property such as the electrical conductivity of a solid can be understood only as a consequence of the strong interaction between the atoms. This interaction may change the properties of the individual atoms to such an extent that the properties of the solid may be completely different from those of the separate atoms.

In this first chapter we shall present some material which will be used in later chapters. It seems in order, for example, to make some remarks about atoms and their structure, about the arrangement of atoms in solids, and about the interaction between atoms in solids. Since this is not a book on the physics of atoms or a general book on the physics of solids, it may suffice to give here only the most essential elements of these subjects. In the remaining chapters, these subjects will be extended as the need arises.

## 1.2 The hydrogen atom according to the old and new quantum mechanics

There is a vast amount of experimental evidence which shows that an atom consists of a positively charged nucleus and a number of negatively charged electrons which revolve about the nucleus. The nucleus may be considered to be built up of a number of neutral particles (neutrons) and a number of positively charged protons. The charge of the nucleus is thus determined by the number of protons it contains,  $Z$ ; the charge per proton is  $e = 1.60 \times 10^{-19}$  coulomb. In a neutral atom, the number of electrons is equal to  $Z$ , the charge carried by each electron being equal to  $-e$ . The

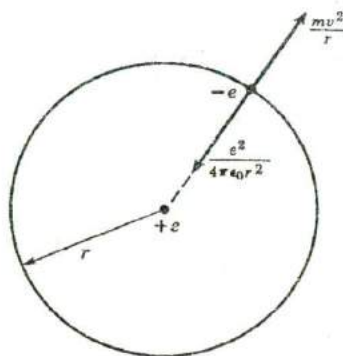


mass of an electron is  $m = 9.107 \times 10^{-31}$  kg, and is approximately 1836 times smaller than that of a proton or a neutron. Hence, practically the whole mass of an atom is concentrated in the nucleus.

The size of an atom is not a well-defined quantity, but may be said to be of the order of 1 angstrom =  $10^{-10}$  m. The classical radius of an electron and of a nucleus, on the other hand, is only of the order of  $10^{-15}$  m; consequently, in terms of a classical representation of electrons, an atom is essentially "empty." In terms of the wave mechanical interpretation, however, it is better to think of the electrons revolving about the nucleus as a *continuous charge distribution*. The shape of the charge distribution is determined by the state of motion of the electron. The difference between a semi-classical representation of an electron and the wave mechanical representation may be illustrated by discussing briefly the structure of the hydrogen atom according to the old quantum theory of Bohr (1913), and by comparing this result with that obtained on the basis of wave mechanics (Schrödinger, Heisenberg, 1924).

A hydrogen atom consists of an electron moving in the field of a proton. Assuming the electron revolves as a point-like particle in a circular orbit of radius  $r$  around the proton, the stability of the orbit requires equilibrium

Fig. 1.1. Illustrating the forces corresponding to a circular orbit of an electron in a hydrogen atom.



between the attractive Coulomb force on the electron and the centrifugal force. Hence, we must require with reference to Fig. 1.1

$$\frac{mv^2}{r} = \frac{e^2}{4\pi\epsilon_0 r^2} \quad (1.1)$$

Here,  $v$  is the velocity of the electron in the orbit and  $\epsilon_0 = 8.854 \times 10^{-12}$  farad  $\text{m}^{-1}$ . The total energy of the electron,  $W$ , in this state of motion is equal to the kinetic energy,  $(1/2)mv^2$ , plus the potential energy due to the Coulomb field of the proton. Defining the potential energy of the electron

for  $r \rightarrow \infty$  as zero, we thus may write

$$W = \frac{1}{2}mv^2 - \frac{e^2}{4\pi\epsilon_0 r} \quad (1.2)$$

Substituting for  $(1/2)mv^2$  from (1.1) into (1.2) we obtain

$$W = -\frac{e^2}{8\pi\epsilon_0 r} \quad (1.3)$$

The minus sign indicates that the electron has less energy in the orbit  $r$  than it would have if  $r$  were infinite. In other words, the electron is bound in the field of the nucleus, the energy required to take it away from the nucleus being equal to the positive quantity  $-W$ . Up to this point, the treatment falls completely within the realm of classical physics. However, it is well known that this classical atomic model is unstable because the energy would decrease continually as a result of emission of electromagnetic radiation; ultimately, the electron would spiral into the nucleus. In order to retain the stability of the orbit, Bohr postulated a *quantum condition* on the motion of the electron by assuming that only those circular orbits are stable for which the angular momentum is equal to an integer times  $h/2\pi$ , where  $h = 6.62 \times 10^{-34}$  joule sec represents Planck's constant. Mathematically this quantum condition for a circular orbit reads

$$mvr = n\hbar/2\pi \quad \text{where } n = 1, 2, 3, \dots \quad (1.4)$$

On the basis of this postulate one finds a set of energy levels  $W_n$  which the orbiting electron may assume. Thus, by substituting for  $v^2$  from (1.4) into (1.1) one obtains for the possible radii of the circular orbits

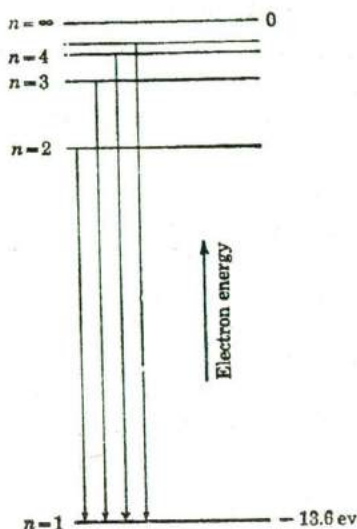
$$r_n = \frac{\epsilon_0 \hbar^2}{\pi m e^2} n^2 = 0.529 \times 10^{-10} n^2 \text{ meter} \quad (1.5)$$

Thus, the smallest radius the electron orbit can assume is 0.529 angstroms; the next possible radii are 4, 9, 16, etc. times as large. In accordance with (1.3) this means that the energy of the electron can accept only a *series of discrete values*,  $W_n$ , given by

$$W_n = -\frac{me^4}{8\epsilon_0^2 \hbar^2} \frac{1}{n^2} = -\frac{13.6}{n^2} \text{ electron volts} \quad (1.6)$$

(One electron volt = 1 ev =  $1.6 \times 10^{-19}$  joule.) Thus, in its lowest state (the *ground state*) the electron is bound to the field of the proton to the extent of 13.6 ev, i.e. it takes an energy of 13.6 ev to ionize the hydrogen atom. The energy levels are represented schematically in Fig. 1.2. As explained in some detail in courses on atomic physics, this energy level diagram agrees satisfactorily with certain parts of the emission and absorption spectra of

Fig. 1.2. Energy levels of an electron in a hydrogen atom; the levels for  $n > 5$  have not been indicated. The vertical arrows indicate transitions from higher levels to the ground state; these transitions correspond to emission of electromagnetic radiation.



hydrogen, if one makes the further postulate that a transition of the electron from an energy level  $W_{n_1}$  to another level  $W_{n_2}$  is associated with the emission or absorption of electromagnetic radiation of a frequency  $\nu$  such that

$$h\nu = |W_{n_1} - W_{n_2}| \quad (1.7)$$

The *ad hoc* postulate of Bohr expressed by equation (1.4) obtains a definite physical meaning when considered in the light of *wave mechanics*. We shall not enter into this subject here, and it may suffice to make some general remarks. In wave mechanics, particles are described by waves; the intensity of the waves in a certain volume element in space is interpreted as representing the probability of finding the particle in this volume element. Thus, wave mechanics is *statistical* in the sense that it does not give a definite answer as to where the particle "is" at a certain instant; it tells us only what the *probability* is of finding it in a certain small volume element in space. Consequently, in describing an electron in an atom in terms of wave mechanics one ends up with a certain *charge distribution* of a "smeared-out" electron. The *wave function*, which represents these waves and hence determines the charge distribution associated with the electron, satisfies the so-called *Schrödinger wave equation*. This equation is a partial differential equation which replaces the classical Newtonian equations of motion. When applied to the problem of an electron moving in the field of a proton, it turns out that physically acceptable solutions for the wave



function exist only for specific integer values of three quantum numbers:

$$\text{the principal quantum number } n = 1, 2, 3, \dots \quad (1.8)$$

$$\text{the angular momentum quantum number } l = 0, 1, \dots, (n - 1) \quad (1.9)$$

$$\text{the magnetic quantum number } m_l = l, (l - 1) \dots, -(l - 1), -l \quad (1.10)$$

In quantum mechanics then, the quantum numbers arise as a natural consequence of the *wave nature of matter*; for a discussion of the experimental evidence which supports this notion, we refer the reader to textbooks on the subject. The principal quantum number fulfills the same role as the quantum number  $n$  in the theory of Bohr; i.e., the energy levels obtained from wave mechanics are the same as those given by the Bohr formula (1.6). As a result of the wave nature of the electrons, however, the interpretation of the motion of the electron in the ground state in terms of a circular orbit in the Bohr theory is replaced by an interpretation in terms of a charge distribution in the wave mechanical theory. For example, the charge density associated with an electron moving about the nucleus in the ground state of a hydrogen atom is given by

$$\rho(r) = -(e/\pi r_1^3) e^{-2r/r_1} \quad (1.11)$$

where  $r_1$  is equal to 0.529 angstroms, i.e.  $r_1$  is equal to the radius of the first Bohr orbit; see Fig. 1.3(a). The total charge corresponding to this charge

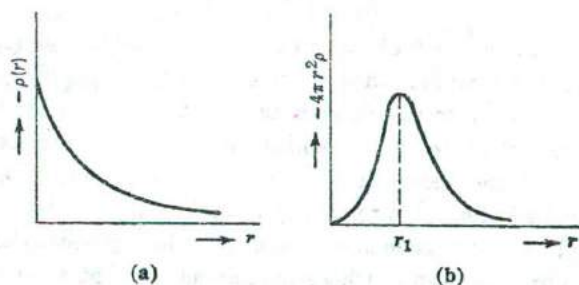


Fig. 1.3. A schematic representation of the electronic charge density  $\rho(r)$  of a hydrogen atom in the ground state is given in (a). In (b) the integrand of expression (1.12) is represented schematically;  $r_1$  is the first Bohr radius of the hydrogen atom.

distribution is, of course, equal to the electronic charge; i.e.

$$\int_{r=0}^{\infty} 4\pi r^2 \rho(r) dr = -e \quad (1.12)$$

as may readily be verified by the reader. The amount of charge contained in a shell between two concentric spheres of radii  $r$  and  $r + dr$  is presumably

given by the integrand in expression (1.12). The integrand has its maximum value for  $r = r_1$ , as indicated in Fig. 1.3(b). Hence, in the wave mechanical theory, the maximum of the charge distribution in the ground state occurs for a distance from the nucleus equal to the first Bohr radius.

The quantum number  $l$  determines the angular momentum of the electron, whereas  $m_l$  determines the *component* of the angular momentum along a prescribed direction, which may be, for example, the direction of an external magnetic field. The physical meaning of these quantum numbers will be discussed further in the chapter dealing with the magnetic properties of atoms.

### 1.3 Nomenclature pertaining to electronic states

In the preceding section it was noted that the state of motion of the electron in a hydrogen atom can be described by three quantum numbers  $n$ ,  $l$  and  $m_l$ , and a set of these numbers is said to define the *state* of the electron. In the lowest energy level ( $n = 1$ ) the quantum numbers  $l$  and  $m_l$  must both be zero in accordance with the rules (1.9) and (1.10). Thus, the ground state of the hydrogen atom is defined by  $n = 1$ ,  $l = 0$  and  $m_l = 0$ . If the electron is in a higher energy level, say in the level corresponding to  $n = 2$ , various states are possible. In fact, by applying the rules (1.9) and (1.10) we find the possible states

$$\begin{array}{lll}
 n = 2 & l = 0 & m_l = 0 \\
 n = 2 & l = 1 & m_l = 1 \\
 n = 2 & l = 1 & m_l = 0 \\
 n = 2 & l = 1 & m_l = -1
 \end{array} \tag{1.13}$$

Each of these states corresponds to a particular charge distribution of the "smeared-out" electron in wave mechanics. In atomic physics, states with a particular  $l$ -value have a particular name. Thus, a state with  $l = 0$  is called an "s-state"; a state with  $l = 1$  is called a "p-state," etc. These names are derived from the nomenclature used in the classification of spectral lines of atoms. We give here the names for the states corresponding to various values of  $l$ :

$$\begin{array}{cccccc}
 l = 0 & 1 & 2 & 3 & 4 & \dots \\
 \text{name the} & & & & & \\
 & s & p & d & f & g \dots \text{-states}
 \end{array} \tag{1.14}$$

We may now raise the question: for a given value of the principal quantum number  $n$ , how many electronic states are possible? Presumably, what we are asking for is the number of different sets of  $n$ ,  $l$ ,  $m_l$  values which exist



for a given value of  $n$ , assuming that the quantum numbers satisfy the rules (1.9) and (1.10). To answer this question, we first note that according to (1.10) there are  $(2l + 1)$  possible values of  $m_l$  for a given value of  $l$ . Furthermore, according to (1.9)  $l$  can accept a total of  $n$  different values for a given value of  $n$ . Hence, the total number of states corresponding to a given value of  $n$  is equal to

$$\sum_{l=0}^{l=n-1} (2l + 1) = 1 + 3 + \dots [2(n - 1) + 1] = n^2 \quad (1.15)$$

Thus, for  $n = 2$ , there are  $2^2 = 4$  different states, which is confirmed by the result in (1.13); for  $n = 3$ , there are 9 different states, etc. It is emphasized that an *energy level is not equivalent with an electronic state*; an energy level is determined by the value of  $n$ , and such a level thus corresponds to  $n^2$  states. It should be mentioned here that actually the energy of an electron is also determined to some extent by the quantum numbers  $l$  and  $m_l$ ; however, the differences in energy between an electron in the state,  $n, l_1, m_{l1}$ , and an electron in the state  $n, l_2, m_{l2}$  is very small compared to the energy difference between two states of different  $n$ -values.

The group of states corresponding to a given value of the principal quantum number  $n$  is referred to as a *shell* of electrons. Thus, the states corresponding to  $n = 1$  form the *K-shell*; those corresponding to  $n = 2$  form the *L-shell*, etc. Hence,

$$n = 1 \quad 2 \quad 3 \quad 4 \quad 5 \quad \dots$$

correspond to the

$$K \quad L \quad M \quad N \quad O \quad \dots \text{-shells}$$

## 1.4 The electron configuration of atoms

In an atom containing more than one electron, the nomenclature given for the electronic states is retained. In determining the states of the electrons in a many-electron atom, the *Pauli exclusion principle* must be introduced. This principle says that *a given quantum state determined by three quantum numbers  $n, l, m_l$  can be occupied by not more than two electrons.*\* For example, the *K-shell* of an atom corresponds to  $n = 1$  and thus contains only 1 state, viz.  $n = 1, l = 0$  and  $m = 0$ . According to the Pauli exclusion principle, there can be no more than 2 electrons in the *K-shell*. Similarly, the *L-shell*, corresponding to  $n = 2$  has 4 different sets of values  $n, l, m_l$  and hence can contain no more than  $2 \times 4 = 8$  electrons. In gen-

\* The factor 2 arises from the *spin quantum number,  $s$* , which can accept two possible values; for further details, see section 4.8.



eral, the electron shell corresponding to the principal quantum number  $n$  can contain no more than  $2n^2$  electrons.

These rules are important for the interpretation of the periodic system of the elements in terms of the electron configuration of the atoms. For

Table 1.1. THE ELECTRON CONFIGURATION OF THE FIRST 36 ELEMENTS

Atomic Number $Z$	Element	K $n = 1$		L $n = 2$		M $n = 3$			N $n = 4$				
		$l = 0$	$l = 0$	$l = 1$	$l = 0$	$l = 1$	$l = 2$	$l = 0$	$l = 1$	$l = 2$	$l = 3$		
		$s$	$s$	$p$	$s$	$p$	$d$	$s$	$p$	$d$	$f$		
1	H	1											
2	He	2											
3	Li	2	1										
4	Be	2	2										
5	B	2	2	1									
6	C	2	2	2									
7	N	2	2	3									
8	O	2	2	4									
9	F	2	2	5									
10	Ne	2	2	6									
11	Na	2	2	6	1								
12	Mg	2	2	6	2								
13	Al	2	2	6	2	1							
14	Si	2	2	6	2	2							
15	P	2	2	6	2	3							
16	S	2	2	6	2	4							
17	Cl	2	2	6	2	5							
18	A	2	2	6	2	6							
19	K	2	2	6	2	6			1				
20	Ca	2	2	6	2	6			2				
21	Sc	2	2	6	2	6	1		2				
22	Ti	2	2	6	2	6	2		2				
23	V	2	2	6	2	6	3		2				
24	Cr	2	2	6	2	6	5	1	2				
25	Mn	2	2	6	2	6	5	2	2				
26	Fe	2	2	6	2	6	6	2	2				
27	Co	2	2	6	2	6	7	2	2				
28	Ni	2	2	6	2	6	8	2	2				
29	Cu	2	2	6	2	6	10	1	2				
30	Zn	2	2	6	2	6	10	2	2				
31	Ga	2	2	6	2	6	10	2	2	1			
32	Ge	2	2	6	2	6	10	2	2	2			
33	As	2	2	6	2	6	10	2	2	3			
34	Se	2	2	6	2	6	10	2	2	4			
35	Br	2	2	6	2	6	10	2	2	5			
36	Kr	2	2	6	2	6	10	2	2	6			

further reference we give in Table 1.1 the electron configuration of a number of atoms. This table shows that up to element 19 (potassium), the filling of the electronic states is completely regular in the sense that higher levels are not filled until lower levels are occupied by the maximum allowable number of electrons. In the element potassium, however, we note that the  $4s$ -level contains one electron while the  $3d$ -states are still unoccupied ( $4s$  means  $n = 4, l = 0$ ;  $3d$  means  $n = 3, l = 2$ ). This situation of incompletely filled  $3d$ -states persists until in element 29 (copper) the  $3d$ -states are occupied by the maximum number of electrons, viz. 10. A group of elements for which parts of an inner shell are not occupied by electrons is called a group of *transition elements*. The particular group for which the  $3d$ -states are partly empty is called the iron group. In the chapter dealing with the magnetic properties of materials we shall see that these properties are determined to a large extent by the incompletely filled inner states.

Our knowledge concerning the electron configuration of atoms has contributed a great deal to the understanding of the periodicity of the chemical properties as expressed by the arrangement of the elements in the *periodic table*. The reason is that the *chemical properties of atoms are determined mainly by the outer electron configuration*. Thus, elements such as the alkali metals (Li, Na, K, Rb and Cs) all have one outer electron, and all behave chemically in a similar fashion. The reason for the important role played by the outer electrons in determining the chemical properties of atoms is readily understood. When an atom A is brought close to another atom B, the electrons in the A atom will be subjected to forces which were not present in the absence of B. However, the inner electrons in the A atom are under influence of the strong Coulomb field produced by the nucleus of atom A and hence the perturbing fields produced by atom B are of much less consequence than they are for the more weakly bound outer electrons. The perturbing fields may thus distort the charge distribution of the outer electrons of A and B atoms to such an extent that a *chemical bond* may result. The nature of the chemical bond will be discussed briefly in the next section.

### 1.5 The nature of the chemical bond and the classification of solids

Although we do not intend to discuss the nature of the various kinds of chemical bonds in any detail here, a few general remarks may be in order because the type of bonding between atoms determines to a large extent the electrical and other physical properties of solid materials. From a

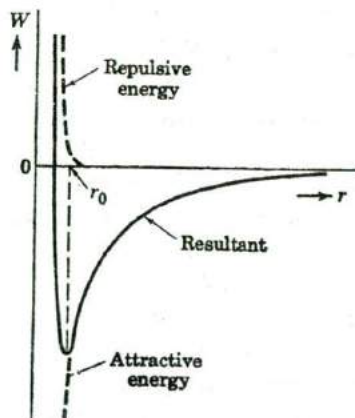


purely phenomenological point of view, we may argue that in a solid material there are two types of forces acting between the atoms: (a) *attractive forces*, which keep the atoms together so as to form a solid, (b) *repulsive forces* which become noticeable when one attempts to compress a solid. These arguments apply as well to liquids and, in fact, to single molecules. It is important to realize, however, that the mere existence of attractive and repulsive forces between atoms is not sufficient to guarantee the formation of a stable chemical bond. This may be illustrated by considering the following model: Suppose two atoms A and B exert attractive and repulsive forces on each other such that the potential energy of B in the field of A is given by

$$W(r) = -\frac{\alpha}{r^n} + \frac{\beta}{r^m} \quad (1.16)$$

where  $r$  is the distance between the centers of the atoms;  $n$  and  $m$  are arbitrary positive powers, and  $\alpha$  and  $\beta$  are positive constants which determine the strength of the attractive and repulsive forces, respectively. The zero of energy is chosen such that for  $r \rightarrow \infty$ , the potential energy of the particles in each other's field vanishes. For the moment we are not concerned about the physical origin of these forces. The question is, will these particles form a stable chemical compound or not? The answer is, that this will only be the case if the function  $W(r)$  exhibits a minimum for a finite value of  $r$ , as illustrated in Fig. 1.4. If such a minimum exists, the two

Fig. 1.4. Representation of the potential energy between two atoms as a function of their distance from one another. The stable molecule corresponds to the separation  $r_0$ , the energy then being a minimum.



atoms will form a stable compound with a distance between them equal to the value  $r_0$  for which the minimum in  $W(r)$  occurs; the energy required to dissociate the molecule is then equal to the positive quantity  $-W(r_0)$ . In order for  $W(r)$  to exhibit a minimum, the powers  $n$  and  $m$  in (1.16) must

satisfy a certain condition, viz.

$$m > n \quad (1.17)$$

In other words, the attractive forces must vary more slowly with  $r$  than the repulsive forces. Qualitatively, this is evident from the shape of the attractive and repulsive energy in Fig. 1.4. Mathematically, this can be shown as follows: If  $W(r)$  exhibits a minimum for  $r = r_0$ , then we must require

$$(dW/dr)_{r=r_0} = 0 \quad \text{or} \quad r_0^{m-n} = (m/n)(\beta/\alpha) \quad (1.18)$$

and at the same time

$$\left(\frac{d^2W}{dr^2}\right)_{r=r_0} = -\frac{n(n+1)\alpha}{r_0^{n+2}} + \frac{m(m+1)\beta}{r_0^{m+2}} > 0 \quad (1.19)$$

The condition (1.17) then follows immediately by substituting  $r_0$  from (1.18) into (1.19).

The forces acting between atoms are of an electrostatic nature and, as mentioned in the preceding section, are determined essentially by the extent to which the wave functions of the outer electrons are perturbed by the presence of other atoms at close proximity. On the basis of the type of chemical bond, solids may be classified as follows:

- (i) Ionic crystals (NaCl, KF)
- (ii) Valence crystals (diamond, Si, Ge, SiC)
- (iii) Metals (Cu, Ag, Fe)
- (iv) van der Waals crystals (solid argon, organic crystals)

With reference to each of these classes we shall now make some general remarks concerning the chemical bonds in these materials.

(i) **Ionic crystals.** Ionic crystals are formed by combining two or more kinds of atoms which differ considerably in their tendencies to give off or to accept electrons. For example, when sodium and chlorine atoms are combined, the energy of the solid in which the sodium atoms become positive ions and the chlorine atoms become negative ions is lower than that in which the atoms remained neutral. The outer 3s electrons of the sodium atoms are transferred to the chlorine atoms which thereby obtain a stable configuration of 6 electrons in the 3p-states. Now, the ionization of a free sodium atom requires an energy of 5.1 ev, whereas the energy gained by putting an electron on a neutral Cl atom is 4 ev. One might get the impression that transfer of an electron from sodium to chlorine is unfavorable in the sense that the net energy expended is positive. This is indeed the case if the two atoms are a great distance apart. However, when the Na<sup>+</sup> ion and the Cl<sup>-</sup> ion are brought together so that their nuclei are separated by only a few angstroms, *energy is gained as a result of the Coulomb attrac-*



*tion between the ions.* Thus, in the solid state, sodium chloride is built up of  $\text{Na}^+$  and  $\text{Cl}^-$  ions, rather than of neutral atoms. The Coulomb forces between these ions are mainly responsible for keeping the ions together. Since the electrons in these ions are all rather tightly bound, ionic crystals exhibit in general, no electrical conductivity which can be associated with the motion of electrons. However, at elevated temperatures they do show some electrical conductivity associated with the motion of ions under influence of an electric field.

Ionic solids are formed particularly between elements on the left- and on the right-hand sides of the periodic table. Thus, the alkali halides formed between the alkali metals Li, Na, K, Rb, Cs and the halogens  $\text{F}_2$ ,  $\text{Cl}_2$ ,  $\text{Br}_2$ ,  $\text{I}_2$  are strongly ionic. On the other hand, a compound such as BaS is probably somewhat less ionic; i.e., the barium atoms do not part completely from their two outer valence electrons. Taking an element such as In from the third column in the periodic table and an element such as Sb from the fifth column gives rise to a compound (in this case indium antimonide) which has very little ionic character at all. These remarks indicate that the classification given above refers to extreme cases and that many solids must be considered as having a chemical bond which lies somewhere between groups (i) and (ii), for example.

Many truly ionic crystals, such as the alkali halides, are transparent for visible light. This property can also be explained in terms of the electron configuration of the material.

(ii) **Valence crystals.** In valence crystals such as diamond, silicon and germanium, the atoms remain neutral. This is not surprising for elements because all atoms are equivalent and there is no reason to assume that some would be ionized while others were not. In a case such as silicon carbide, the atoms are still predominantly neutral, even though they are of different kinds. However, in the case of silicon carbide there may be a slight ionicity involved in the bond because the atoms are different. In a true valence crystal, the binding between the atoms is accomplished by the *sharing of valence electrons*. This will be discussed further in the chapter on semiconductors. These valence or homopolar bonds can be understood only in terms of a wave mechanical theory. In principle, this type of bond is similar to that which exists between two hydrogen atoms in a hydrogen molecule. Valence bonds can be extremely strong, as witnessed by the hardness of materials such as diamond or carborundum.

(iii) **Metals.** In metals the valence electron wave functions are so strongly perturbed by the presence of neighboring atoms that the sharing of these electrons goes so far as to make them highly mobile. In other

words, the *valence electrons in a metal cannot be associated with particular atoms; they belong to all atoms.* There is a resemblance between valence crystals and metals because in both cases valence electrons are shared with other atoms. However, in a valence crystal the valence electrons are shared only between nearest neighbor atoms, whereas in a metal the valence electrons are shared by all atoms. Thus, a metal may be considered to consist of an assembly of positive ions embedded in a sea of negative valence electrons. The attractive forces which keep the atoms together arise mainly as a consequence of the Coulomb attraction between the system of positive ions and the negative charge distribution corresponding to the valence electrons. The similarity between valence bonds and metallic bonds will be discussed further in the chapter dealing with semiconductors. It will be argued there that if one considers the elements in the fourth column of the periodic system in the order: diamond, silicon, germanium, gray tin, and lead, one finds a *gradual transition from an extreme valence bond in diamond to a metallic bond in lead.*

(iv) *van der Waals crystals.* It is well known that the atoms of the rare gases such as helium, argon, and neon are chemically extremely inactive; they form no compounds with other atoms. In other words, the outer electron wave functions are not easily perturbed by the presence of other atoms. This chemical inactivity indicates a high degree of stability of the outer electron shell. This is also the reason why these materials remain in the gaseous state at normal temperatures. At very low temperatures, however, a gas like argon will form a solid and the question arises as to what keeps these chemically inactive atoms together. In terms of a classical picture, these weak attractive forces arise as a consequence of the fact that an electron revolving around a nucleus may be considered to represent a rotating electric dipole. Such a dipole will induce a dipole in a neighboring atom such that a dipole-dipole attraction between the atoms results. The process by which a dipole is induced in an atom by means of an electric field will be discussed in detail in the chapter on dielectrics. From a mathematical analysis of the forces acting between neutral atoms it follows that, besides the dipole-dipole interaction just mentioned, there are higher order interactions of the kind dipole-quadrupole, quadrupole-quadrupole, etc. All these forces together are referred to as *van der Waals forces.*

The same kind of forces act between neutral molecules; i.e., many organic molecules form aggregates in which the molecules are held together by van der Waals forces.

A summary of the classification above is given in Fig. 1.5. Starting in the upper left-hand corner, we find metals in which the valence electrons



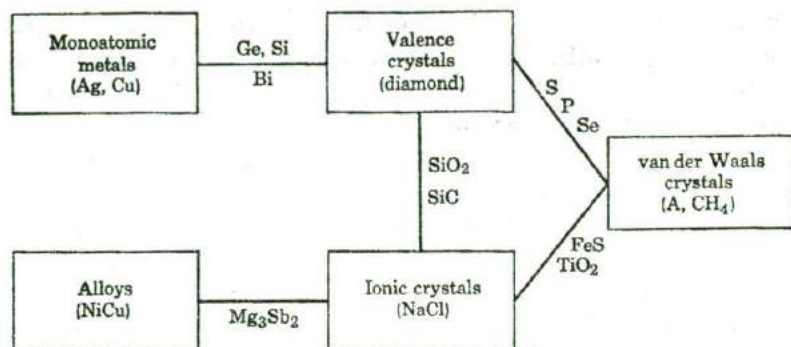


Fig. 1.5. Classification of solids; see text.

are shared by all atoms. Related to this group are the valence crystals in which the valence electrons are shared by nearest neighbors. Intermediate, between these two cases are, at least at room temperature, the semiconducting elements such as Ge and Si. At absolute zero, Ge and Si belong in the class of true valence crystals, as we shall see in the chapter on semiconductors. There are also cases which may be considered intermediate between valence and van der Waals solids, such as sulfur, phosphorus, and selenium. Going now to the lower left-hand corner of Fig. 1.5 we see metallic alloys such as nickel-copper. If two metals A and B differ chemically to an appreciable extent, the A atoms may have the tendency to become positive ions whereas the B atoms may have the tendency to become negative ions. Thus, an alloy of magnesium and antimony forms a rather definite compound of chemical composition  $Mg_3Sb_2$ , corresponding to  $Mg^{2+}$  and  $Sb^{3-}$  ions, although it is by no means a purely ionic compound. A case like this is intermediate between an alloy and an ionic crystal. Intermediate between ionic crystals and valence crystals are compounds such as SiC and  $SiO_2$ ; here the bonds are partly ionic and arise partly from the sharing of electrons. Materials such as FeS and  $TiO_2$  are intermediate between ionic and van der Waals crystals. Thus, we may have ionic bonds in layers of atoms, the layers being held together partly by van der Waals forces.

## 1.6 Atomic arrangements in solids

Most solids to be discussed in this book are *crystalline*; i.e., the atoms or ions are stacked in a regular manner. The fact that a material is crystalline does not necessarily imply that this regular stacking extends throughout the volume of a macroscopic specimen. In fact, one generally deals

with *polycrystalline* materials consisting of grains within which the atomic arrangement is essentially regular, but showing irregularities as one goes from one grain to another through the so-called grain boundaries. These grains may be small, say  $10^{-6}$  m in diameter, or large. If the atoms are stacked in a regular manner throughout a macroscopic specimen, one speaks of a *single crystal*. It should be mentioned here that even in a single crystal or inside a single grain, there are always certain irregularities or defects. Thus, in general there will be atoms missing at places where they ought to occur in a perfect crystal; one refers to such defects as *vacant lattice sites*. Similarly, there is always a certain number of atoms which occupy positions which in a perfect crystal should not be occupied; such atoms are referred to as *interstitial atoms*. In many cases these defects are very important in explaining the physical properties of materials. For example, the *ionic conductivity* of the alkali halides is due to the presence of vacant lattice sites; if there were no vacant lattice sites, the ions could not move about and the ionic conductivity would be zero at all temperatures. Similarly, in ionic crystals and in metals *diffusion* of atoms takes place by virtue of the presence of vacant lattice sites or interstitial atoms.

Besides the defects just mentioned, there are, of course, always a certain number of foreign atoms present in a material. These impurities may determine to a large extent certain physical properties of the material. This is most dramatically illustrated in the case of *semiconductors*, where the electrical conductivity may be changed by several orders of magnitude by the addition of a fraction of a percent of certain impurities. This subject will be discussed in some detail in Chapter 6. Then there are defects known as *dislocations*; these defects are responsible for the *plastic deformation* of materials. We shall not discuss this subject here, and the reader is referred to the literature on the subject. From these remarks it is evident that an important part of the study of materials is concerned with the study of lattice imperfections. In this section, however, we are concerned not so much with the imperfections as with the regularity of the atomic arrangements in "perfect" crystals.

The most characteristic property of a crystal is its *periodicity of structure*. By this we mean that a crystal may be considered as a repetition in three dimensions of a certain unit pattern, much as certain types of wallpaper have this property in two dimensions. It is not our intention to go into any details concerning crystal structures because it is not necessary for the kind of discussion given in subsequent chapters. It may suffice to give a few examples. In Fig. 1.6 we have presented the crystal structure of NaCl; this structure is typical of the alkali halides, except for the rubidium and



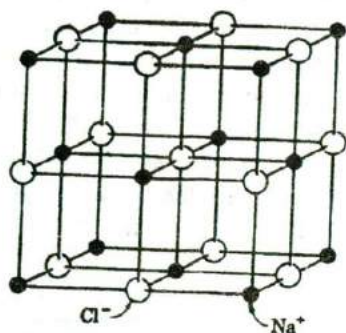


Fig. 1.6. The structure of NaCl.

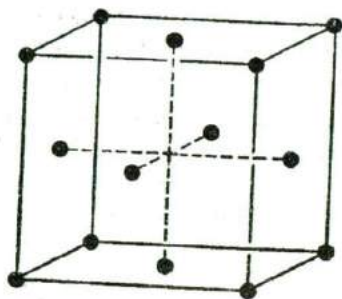


Fig. 1.7. The face-centered cubic lattice.

cesium salts. The dots and circles represent the positions of the  $\text{Na}^+$  and  $\text{Cl}^-$  nuclei. In an actual crystal neighboring ions "touch" each other and are thus much larger than indicated by the circles and dots (apart from the scaling factor!). It is observed that the  $\text{Na}^+$  ions occupy the corners of a cube as well as the centers of the cube faces. Such an arrangement is called *face-centered cubic*. Interwoven with this arrangement is a completely equivalent lattice of  $\text{Cl}^-$  ions. By stacking cubes of this kind in three dimensions; i.e., by repeating the pattern of Fig. 1.6 periodically, a perfect crystal of NaCl would be obtained.

Another example of a face-centered cubic lattice is given in Fig. 1.7, in which all atoms are identical. This is an arrangement found in many metals, such as Cu, Ag, Au, Al, Ni, and a number of others. Several metals crystallize in what is known as a *body-centered cubic structure*, represented in Fig. 1.8; in this case the corners of a cube and the center of the cube are occupied by identical atoms. This structure is found, for example, in Li, Na, K, and Fe.

An example of a somewhat more complicated structure is given in Fig.

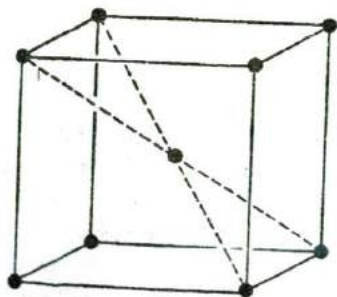
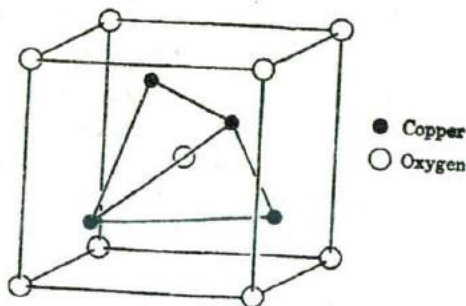


Fig. 1.8. The body-centered cubic lattice.

Fig. 1.9. The structure of  $\text{Cu}_2\text{O}$ .

1.9, for cuprous oxide ( $\text{Cu}_2\text{O}$ ). Here, the oxygen atoms (or ions) satisfy a body-centered cubic arrangement, whereas the copper atoms are arranged at the corners of a tetrahedron around the central oxygen atom.

One may ask: How does one know that the atoms in a given material are arranged in a particular fashion? The answer is that such information can be obtained from *X-ray* or *electron diffraction patterns*. The principle of X-ray diffraction may be illustrated briefly with reference to Fig. 1.10. The horizontal lines represent planes of atoms in a crystal, the distance

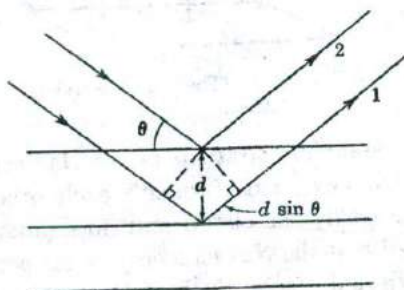


Fig. 1.10. Illustrating Bragg reflection of X-rays by a set of equidistant atomic planes.

between these planes being of the order of a few angstroms. Suppose a monochromatic beam of X-rays of a certain wavelength  $\lambda$  is incident on the set of planes, the angle between the incident beam and the planes being  $\theta$ . If there exists a certain relationship between  $\lambda$ ,  $\theta$ , and the distance  $d$  between successive planes, reflection of the X-ray beam may be observed. In general then, for an arbitrary value of  $\theta$ , assuming  $\lambda$  and  $d$  to be fixed, no reflection will be observed. The condition which  $\theta$  must satisfy in order to observe reflection is evidently that the rays reflected by successive planes are in phase. Thus, if the phase difference between 1 and 2 in Fig. 1.10 is zero, these rays will reinforce each other, and at the same time they will reinforce other rays reflected against deeper lying planes. The condition for reinforcement is clearly that the path difference between 1 and 2 must be equal to an integer times the wavelength of the X-ray beam. Thus,

$$2d \sin \theta = n\lambda \quad \text{where } n = 1, 2, 3, \dots \quad (1.20)$$

By measuring the angles  $\theta$  for which reflection occurs one can thus find the distance between subsequent planes of the set under consideration. From a more detailed analysis one can, in fact, find the arrangement of atoms in the basic unit from which the crystal can be built up. Condition (1.20) is known as the *Bragg condition* for X-ray reflection from a certain set of planes.

Not all materials are crystalline, although for most solids the crystalline state is the natural one because the energy of the ordered atomic arrange-



ment is usually lower than that of an irregular packing of atoms. However, when the atoms are not given the opportunity to arrange themselves in an orderly manner, by inhibiting their mobility during solidification, an *amorphous* material may be formed. This is the case, for example, in the formation of soot. In other cases, the molecules may be extremely long and irregular in shape, so that an orderly arrangement may not be obtained easily, as in the case of polymers. In some materials, such as glass, the solid state corresponds to a *supercooled liquid* in which the molecular arrangement of the liquid state is frozen in. Due to the high viscosity of the liquid, crystals do not have time to grow under normal conditions, and an amorphous material is formed. Upon annealing, such glassy materials may crystallize (*devitrify*), as observed in the case of quartz.

In the remaining chapters we shall have ample opportunity to indicate the importance of the regular or irregular stacking of atoms on the properties of materials.

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C. W. Bunn, *Chemical Crystallography*, Oxford, New York, 1945.  
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### Problems

1.1 Given that one gram molecule of a gas at  $0^{\circ}\text{C}$  and a pressure of 760 mm mercury occupies a volume of 22.414 liters, and assuming Avogadro's number is  $6.025 \times 10^{23}$ , compute the number of molecules per  $\text{m}^3$  in a gas at  $0^{\circ}\text{C}$  and 760 mm mercury (Loschmidt's number).

1.2 A residual pressure of  $10^{-10}$  mm mercury in a vacuum tube is considered very good vacuum; estimate the number of gas molecules per  $\text{m}^3$  in such a tube at room temperature.

1.3 According to the kinetic theory of gases, the average kinetic energy of a gas molecule at an absolute temperature  $T$  is equal to  $(3/2)kT$ , where  $k$  is Boltzmann's constant. What is the average energy, expressed in electron volts, at room temperature ( $T = 300^{\circ}\text{K}$ )? If the gas is hydrogen, what is the order of magnitude of the velocity of the molecules at  $T = 300^{\circ}\text{K}$ ?

1.4 Calculate the velocity of an electron with a kinetic energy of 1 eV; what is the velocity of a proton with a kinetic energy of 1 eV?

1.5 Calculate the kinetic energy, the potential energy, and the total energy of an electron in the ground state of a hydrogen atom according to the theory of Bohr.

1.6 Calculate the energy and radii of the first four Bohr orbits for an electron in a hydrogen atom.

1.7 An electron in a hydrogen atom makes a transition from a quantum state of principal quantum number  $n = 2$  to the ground state. What is the energy and what is the frequency  $f$  of the emitted light quantum? In what region of the electromagnetic spectrum do you place this frequency?

1.8 According to wave mechanics, the wavelength  $\lambda$  of an electron is related to the momentum  $p$  of the electron by means of the so-called de Broglie formula  $\lambda = h/p$ , where  $h$  is Planck's constant. Show that the wavelength of an electron with kinetic energy of  $V$  electron volts is given by  $\lambda = (150/V)^{1/2}$  angstroms.

1.9 Show that Bohr's quantum postulate for circular orbits is equivalent to the statement that the circumference of the orbit is equal to an integer times the wavelength of the electron.

1.10 In an electron-diffraction experiment one wishes to have a wavelength of the electrons of 0.5 angstrom. What accelerating voltage is required to obtain this wavelength?

1.11 According to wave mechanics, the charge distribution corresponding to the electron in the ground state of a hydrogen atom is an exponential function of the type  $\rho(r) = A \exp(-2r/r_1)$  where  $A$  and  $r_1$  are constants and  $r$  represents the distance from the nucleus. Given that the total charge must be equal to  $-e$ , show that  $A = -e/\pi r_1^3$  (see formula 1.11).

1.12 Show that the integrand in formula (1.12) has its maximum value for  $r = r_1$ .

1.13 On the basis of the rules pertaining to the possible values of the orbital and magnetic quantum numbers  $l$  and  $m_l$ , set up a table which gives all possible quantum states for the principal quantum number  $n = 3$  [in analogy with (1.13) for  $n = 2$ ].

1.14 Assume the energy of two particles in the field of each other is given by the following function of the distance  $r$  between the centers of the particles:

$$W(r) = -(\alpha/r) + (\beta/r^8)$$

where  $\alpha$  and  $\beta$  are constants.

(a) Show that the two particles form a stable compound for  $r = r_0 = (8\beta/\alpha)^{1/7}$ .



(b) Show that in the stable configuration the energy of attraction is 8 times the energy of repulsion (in contrast with the fact that the attractive force is equal to the repulsive force!).

(c) Show that the total potential energy of the two particles in the stable configuration is equal to

$$-(7/8)(\alpha^8/8\beta)^{1/7} = -(7/8)\alpha/r_0.$$

(d) Show that if the particles are pulled apart, the molecule will break as soon as  $r = (36\beta/\alpha)^{1/7} = r_0(4.5)^{1/7}$ , and that the minimum force required to break the molecule is equal to

$$[\alpha^{2/7}/(36\beta)^{2/7}][1 - 8/(36)^{2/7}].$$

**1.15** Suppose an atom A has an ionization energy of 5 ev, and an atom B has an electron affinity of 4 ev (i.e., an energy of 4 ev is gained by attaching a free electron to atom B). Suppose atoms A and B are 5 angstroms apart. What is the energy required to transfer an electron from A to B?

**1.16** The edge of the elementary cube of a body-centered cubic lattice is  $a$  meter. How many atoms are there on the average per cube of  $a^3$  meter<sup>3</sup>? Answer the same questions for a face-centered cubic lattice and for a simple cubic lattice (atoms only at the corners of the elementary cube).

**1.17** Suppose identical atoms are arranged in a simple cubic lattice; the atoms may be considered as hard spheres of radius  $R$ . The edge of the elementary cube,  $a$ , is equal to  $2R$  so that neighboring atoms touch each other. Show that the fraction of the volume occupied by atoms is  $\pi/6 = 0.523$ .

**1.18** Consider a body-centered cubic lattice of identical atoms; the atoms may be considered as hard spheres of radius  $R$ . Atoms along a body diagonal touch each other. Show that the fraction of the volume occupied by atoms in this arrangement is  $(\pi\sqrt{3})/8 = 0.68$ .

**1.19** Consider a face-centered cubic lattice of identical atoms with radius  $R$ . Atoms along a face diagonal touch each other. Show that the fraction of the volume occupied by atoms in this arrangement is  $(\pi\sqrt{2})/6 = 0.74$ . (Note that this is the most economical way of stacking identical spheres; compare answers to problems 1.17 and 1.18.)

**1.20** Two kinds of atoms, A and B, form a crystal with the same structure as CsCl. Considering the atoms as hard spheres of radii  $r_a$  and  $r_b$ , show that the atoms along a body diagonal of the elementary cube cannot touch each other if the ratio  $r_a/r_b$  (or  $r_b/r_a$ ) is larger than 1.37.

**1.21** Two elements A and B form a compound AB which crystallizes in the sodium chloride structure. Assuming the atoms may be considered as hard spheres of radii  $r_a$  and  $r_b$ , show that atoms along a cube edge cannot touch each other as soon as the ratio of the radii is larger than 2.44.

**1.22** Copper crystallizes in a face-centered cubic lattice, the cube edge being 3.608 angstroms at room temperature. A single crystal of copper has been cut so that the surface of the crystal is parallel to one of the faces of the elementary cube. A monochromatic beam of X-rays with a wavelength of 1.658 angstroms is incident on the surface of the crystal. Show that the planes parallel to the surface reflect the X-rays if the angle between the beam and the surface is approximately 27 deg or 67 deg.

**1.23** The X-ray beam with a wavelength of 1.658 angstroms mentioned in the preceding problem is obtained by electron bombardment of a nickel target. What is the minimum anode voltage required in the X-ray tube to produce this wavelength? Suppose that instead of X-rays one uses electrons of the same wavelength, what would be the required accelerating voltage? (see problem 1.8).

**1.24** From the data given for copper in problem 1.22, calculate the number of atoms per  $\text{m}^3$  in this material.



## 2

# Dielectric Properties of Insulators in Static Fields

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In this chapter we deal with the behavior of insulators in static fields; their behavior in alternating fields will be discussed in the next chapter. It would undoubtedly be more elegant to start immediately with time-dependent fields, and to treat the static behavior as a particular case corresponding to zero frequency. From the student's point of view, however, there are advantages in dealing with the simpler case first because it gives him a chance to absorb the fundamental concepts at a more leisurely pace. Once these concepts are well understood, the transition to the concept of the complex dielectric constant and its interpretation becomes a good deal easier.

The questions to be discussed in this chapter are of the following nature: What is the relationship between the *macroscopic* measurable dielectric constant and the *atomic structure* of a material? Why do some materials have a high and others a low dielectric constant? Why do the dielectric constants of some materials depend on temperature, whereas in other cases they do not? What happens to the dielectric constant when a substance melts or solidifies? These and other questions will be discussed in terms of simplified atomic "models." These models are not necessarily the best representation of atoms known to physicists, but they serve mainly to illustrate the basic ideas underlying more sophisticated calculations. The first two sections are devoted to the macroscopic theory of the dielectric constant as one finds it expounded in much more detail in

textbooks on field theory. The remainder of the chapter deals with the atomic interpretation of the dielectric constant.

## 2.1 The static dielectric constant

The reader may be reminded at this point of some fundamentals concerning electric fields. One of the most useful theorems in this area is that of Gauss. It states that the total electric flux  $\phi$  emanating from a closed surface is equal to the total charge enclosed by that surface. Denoting the charges enclosed by the surface by  $Q_1, Q_2, \dots, Q_i, \dots, Q_n$ , where the  $Q$ 's may be positive and negative, this theorem may be expressed mathematically by means of a surface integral as follows:

$$\phi = \iint \mathbf{D} \cdot d\mathbf{S} = \sum_{i=1}^n Q_i \quad (2.1)$$

Here,  $\mathbf{D}$  represents the *flux density* in coulombs  $\text{m}^{-2}$  at the center of the surface element represented by the outwardly directed vector  $d\mathbf{S}$ ; the integration extends over the entire closed surface. When one deals with a continuous charge distribution of density  $\rho$  instead of with discrete charges, the sum on the right-hand side of (2.1) must, of course, be replaced by the volume integral of  $\rho$ , the integration extending over the entire volume enclosed by the surface under consideration.

The *electric field strength*  $\mathbf{E}$  in any point of space, i.e. the force per unit charge, is related to the flux density in that point by

$$\mathbf{D} = \epsilon_0 \epsilon_r \mathbf{E} \quad (2.2)$$

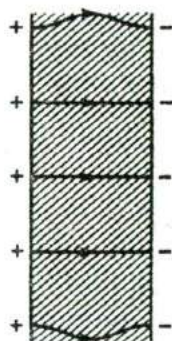
Here,  $\epsilon_0 = 8.854 \times 10^{-12}$  farad  $\text{m}^{-1}$  represents the dielectric constant or permittivity of a vacuum;  $\epsilon_r$  is called the *relative dielectric constant* or the *relative permittivity* of the material. It is important to emphasize that  $\epsilon_0$  enters only as a result of using a particular system of units, in our case mks units;  $\epsilon_0$  therefore has no other physical meaning than that of a fundamental conversion factor. The relative dielectric constant,  $\epsilon_r$ , on the other hand is determined by the atomic structure of the material and it is with the physical interpretation of this quantity that we shall deal below. Note that  $\epsilon_r$  is a dimensionless quantity which is equal to 1 for vacuum. For all substances,  $\epsilon_r > 1$  for reasons that will be explained. It should also be mentioned here that expression (2.2) refers only to *isotropic materials*; i.e., to materials for which the dielectric and other physical properties are independent of the direction in which they are measured. In crystals, for example, the dielectric constant generally depends on the direction along which it is measured relative to the crystal axes. In polycrystalline



materials, on the other hand, with a random distribution of the grains, the directional effects disappear and (2.2) is applicable. For single crystals one cannot, in general, use (2.2) and the dielectric constant should then be replaced by a tensor quantity. Unless stated otherwise, we shall assume isotropic materials. From the fact that  $E$  is expressed in newton coulomb<sup>-1</sup> and from the fact that  $\epsilon_r$  is dimensionless, the reader can readily verify from (2.2) that  $\epsilon_0$  has the dimensions of farad m<sup>-1</sup>.

A method for measuring  $\epsilon_r$  for a particular material emerges from the following reasoning: consider a parallel plate condenser as indicated in Fig. 2.1. The area of the plates is  $A$  and the distance between them  $d$ ;

Fig. 2.1. Charged parallel plate condenser; flux lines are indicated.



assume the charge per unit area on the plates is  $+q$ . Neglecting end-effects, the flux lines run from the positive to the negative plate in a direction perpendicular to the plates. By applying the theorem of Gauss in a suitable manner the reader will readily verify that the magnitude of the flux density is given by  $D = q$ ; this will be true whether or not the space between the plates is filled with an insulating material. It thus follows from (2.2) that the field strength in the region between the plates is given by

$$E = D/\epsilon_0\epsilon_r = q/\epsilon_0\epsilon_r \quad (2.3)$$

Since the voltage difference between the two plates is simply given by  $Ed$  (homogeneous field!), the capacitance of the system is equal to  $C = qA/Ed = \epsilon_0\epsilon_r A/d$ . Hence, if  $C_{vac}$  represents the capacitance when the space between the plates is evacuated, one immediately finds  $\epsilon_r$  from the relation

$$\epsilon_r = C/C_{vac} \quad (2.4)$$

Thus,  $\epsilon_r$  can be determined experimentally by measuring the capacitance with and without the dielectric.

## 2.2 Polarization and dielectric constant

In this section we shall show that in a dielectric subjected to an electric field  $E$ , each volume element may be thought of as carrying an *electric dipole moment* which is proportional to the field strength. As we shall see later, the result obtained is of fundamental importance because it provides a link between the macroscopic dielectric constant and the atomic theory of this quantity.

The electric dipole moment of a neutral system of point charges  $Q_1, Q_2, \dots, Q_i, \dots, Q_n$  is defined as a vector given by

$$\mu = \sum_i Q_i \mathbf{r}_i \quad (2.5)$$

where  $\mathbf{r}_i$  represents a vector drawn from the origin of a coordinate system to the position of the charge  $Q_i$ ; the charges  $Q_i$  may, of course, be either positive or negative, but their sum  $\sum Q_i$  must be zero to comply with the neutrality of the system. As shown in problem 2.8 at the end of this chapter, the vector  $\mu$  is independent of the choice of the origin of the coordinate system; if it were not, it would be a useless concept. In mks units, an electric dipole moment is evidently expressed in coulomb meters. In its simplest form, a dipole moment consists of two equal point charges of opposite sign,  $\pm Q$ , separated by a distance  $d$ . Choosing the origin of the coordinate system to coincide with the negative charge, the dipole moment in this case has a magnitude equal to  $Qd$ , and is represented by a vector pointing from the negative charge in the direction of the positive charge, as indicated in Fig. 2.2.

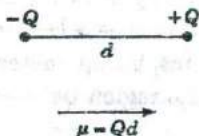
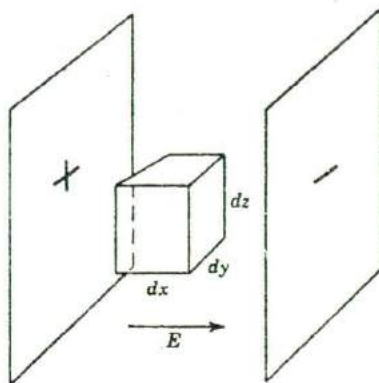


Fig. 2.2. Dipole and dipole moment vector  $\mu$  for two equal charges of opposite sign separated by a distance  $d$ .

Let us now turn to the statement made in the beginning of this section by considering the simple case of a homogeneous and isotropic dielectric subjected to a homogeneous electric field  $E$  produced between two charged parallel plates. Let the flux density be  $D = \epsilon_0 \epsilon_r E$ . Suppose now that we were to cut out of the dielectric a small volume element  $dx \, dy \, dz$  where  $dx$  is chosen perpendicular to the plates, as indicated in Fig. 2.3. This would evidently result in a distortion of the field; i.e., it would no longer be homogeneous. Let us consider the following question: how can the field be kept homogeneous, and equal to the original field  $E$ ? This can be achieved in two ways:



Fig. 2.3. Illustrating a cavity  $dx\ dy\ dz$  cut away from a dielectric between two charged plates.



(a) By inserting the material again in the cavity produced. This answer is trivial, but nevertheless plays a role in the argument, as we shall see later.

(b) In attempting to produce a homogeneous field in the presence of the cavity, we evidently require that if  $E_i$  and  $E_o$  represent the field strengths respectively inside and outside the cavity

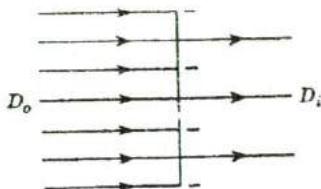
$$E_i = E_o = E$$

Since inside the cavity there is no material, this requirement, when expressed in terms of the flux densities  $D_i$  and  $D_o$  inside and outside the cavity, becomes

$$D_i/\epsilon_0 = D_o/\epsilon_0\epsilon_r = D/\epsilon_0\epsilon_r \quad (2.6)$$

Hence, if the flux density inside the cavity is made  $\epsilon_r$  times as small as the flux density outside the cavity, we have succeeded in making the field homogeneous in the presence of the cavity. Now, according to the theorem of Gauss, a change in flux density at a surface can be achieved only if the surface carries an electric charge. Thus, with reference to Fig. 2.4, if

Fig. 2.4. Illustrating reduction of a flux density  $D_o$  in passing across a plane to the value  $D_i$ , as a result of the presence of negative charges on the surface.



we desire a flux density  $D_o$  to be reduced to a flux density  $D_i$  upon crossing a surface, the surface should be provided with a charge density of  $-(D_o - D_i)$  coulomb  $m^{-2}$ . In our problem, therefore, the field can be made homogeneous by placing a negative charge of  $-(D_o - D_i) dy dz$  on

the left-hand face of the cavity in Fig. 2.3, and a positive charge of  $(D_o - D_i) dy dz$  on the right-hand face. This system of charges is apparently neutral, and corresponds to a dipole moment

$$(D_o - D_i) dx dy dz \quad (2.7)$$

The direction of the dipole moment vector is from left to right in Fig. 2.3, i.e. parallel to the applied field  $\mathbf{E}$ . Now, according to (2.6) we have  $D_o/D_i = \epsilon_r$ , so that (2.7) may be written as

$$D_i(\epsilon_r - 1) dx dy dz = \epsilon_0(\epsilon_r - 1)E dx dy dz \quad (2.8)$$

What conclusion can we draw from these arguments? Since answer (a) achieves the same result as providing the cavity with a dipole moment given by (2.8) we conclude that the material which previously occupied the cavity carried a dipole moment given by (2.8). Thus, a dielectric subjected to a homogeneous field carries a dipole moment  $\mathbf{P}$  per unit volume which, according to (2.8) may be written as

$$\mathbf{P} = \epsilon_0(\epsilon_r - 1)\mathbf{E} \quad (2.9)$$

The dipole moment per unit volume  $\mathbf{P}$  is called the *polarization* of the dielectric. It is expressed in coulomb  $\text{m}^{-2}$  and is proportional to the field strength as long as  $\epsilon_r$  is independent of  $E$ , which it is for normal dielectrics below the breakdown field. It is emphasized that in the derivation of (2.9) nothing was said about the physical state of the dielectric; hence, it is valid for gases, liquids and solids. It will become evident below that (2.9) provides the *link between the macroscopic and atomic theory of dielectrics*.

### 2.3 The atomic interpretation of the dielectric constant of monoatomic gases

The simplest, though for most purposes not the most practical, kinds of materials are the rare gases such as helium and argon. These gases are simple from a theoretical point of view because, first of all, in a gas the average distance between the atoms or molecules is large enough so that one can neglect interaction between them, and furthermore, if we restrict ourselves to the rare gases, the molecules consist of single atoms. Forgetting for the moment the discussion of the preceding two sections, let us consider the problem from the atomic point of view and investigate what can be said about the properties of a rare gas when it is subjected to an electric field  $E$ . First consider a single atom consisting of a positive nucleus of charge  $Ze$ , and  $Z$  electrons moving around the nucleus. Since



the nucleus has a diameter of the order of  $10^{-15}$  m, whereas the radius of the electron cloud is of the order of  $10^{-10}$  m, we may consider the nucleus for our purpose as a point charge. As a crude model for the electron cloud, let us assume that the total negative charge  $-Ze$  is distributed homogeneously throughout a sphere of radius  $R$ , where  $R \approx 10^{-10}$  m

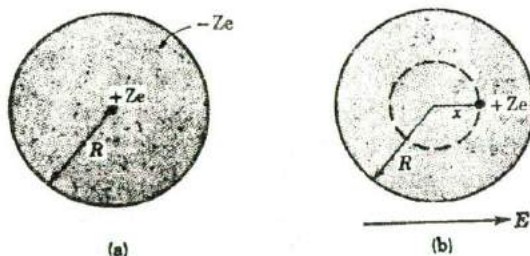


Fig. 2.5. Atomic model in the absence of a field is given in (a); the shift of the negative charge cloud relative to the nucleus resulting from the field  $E$  is presented schematically in (b). In practice,  $x \ll R$ .

[see Fig. 2.5(a)]. Although this model is a far cry from what one knows about atoms, the results that we obtain give the correct order of magnitude for the quantities of interest. When this atomic model is placed in the field  $E$ , the nucleus and the electric cloud will evidently try to move in opposite directions because of the opposite signs of their charges. However, as they are pulled apart, a force will develop between them which tends to drive the nucleus back to the center of the sphere. Consequently, an equilibrium will be obtained in which the nucleus is shifted slightly relative to the center of the electron cloud in the direction of  $E$ . Quantitatively, this shift may be calculated for this model as follows: assume that in equilibrium with the field  $E$ , the nucleus is displaced by the amount  $x$  as indicated in Fig. 2.5(b); we shall assume here that the shape of the electron cloud is not influenced by the field; i.e., it is assumed to remain a sphere of radius  $R$ . The force on the nucleus along the field direction is  $ZeE$ . The electron cloud can be divided into two regions: one inside an imaginary sphere of radius  $x$ , and one between the two spherical surfaces of radii  $x$  and  $R$ . By applying Gauss theorem, the reader will readily verify that the charge in the latter region does not exert a force on the nucleus. The only force exerted on the nucleus is that produced by the negative charge inside the sphere of radius  $x$ ; the charge inside this sphere is equal to  $-Zex^3/R^3$ . The force exerted by this charge on the nucleus can be obtained by concentrating the charge in the center and applying

Coulomb's law; since the total force on the nucleus must be zero in equilibrium, we obtain

$$ZeE = \frac{1}{4\pi\epsilon_0} \frac{(Ze)(Zex^3/R^3)}{x^2} \quad (2.10)$$

Hence, in equilibrium the nucleus will be displaced relative to the center of the sphere by the amount

$$x = (4\pi\epsilon_0 R^3 / Ze) E \quad (2.11)$$

Note that  $x$  is proportional to the field strength and that the problem dealt with is analogous to that in which a mechanical force is exerted on a particle bound with an elastic force to a certain equilibrium position.

What have we learned by deriving (2.11)? In order to see this, consider first the atom in the absence of the field  $E$ . If we were to probe the space outside the atom with an infinitesimally small test charge, we would detect no field at all, because the system is neutral and has no dipole moment (nucleus coincides with the center of the negative charge cloud!). In the presence of the field, the system is still neutral, but has a non-zero dipole moment because the nucleus and the center of the charge cloud are separated by a distance  $x$ . The atom will thus appear to carry a dipole moment (see section 2.2) equal to

$$\mu_{\text{ind}} = Zex = 4\pi\epsilon_0 R^3 E = \alpha_e E \quad (2.12)$$

Here, the subscript "ind" refers to the word "induced"; the dipole moment is induced by the field because it was not there in the absence of the field. The induced dipole moment is proportional to the field strength and the proportionality factor  $\alpha_e$  is called the *electronic polarizability* of the atom; "electronic," because the dipole moment results from a shift of the electron cloud relative to the nucleus. Note that  $\alpha_e$  is proportional to  $R^3$ , i.e. to the volume of the electron cloud.

So far, we have considered only a single atom. Consider now a rare gas containing  $N$  atoms per  $\text{m}^3$ , subjected to a homogeneous field  $E$ . Neglecting any interaction between the dipoles induced in the atoms, which is a good approximation for a gas, we find for the polarization of the gas, i.e. the electric dipole moment per unit volume

$$\mathbf{P} = N\alpha_e \mathbf{E} \quad (2.13)$$

Comparing this expression with the macroscopic equation (2.9) for  $\mathbf{P}$ , we conclude that for rare gases

$$\epsilon_0(\epsilon_r - 1) = N\alpha_e \quad (2.14)$$

In other words, we have obtained a relationship between the measurable quantity  $\epsilon_r$  and the atomic constant  $\alpha_e$ . Let us now investigate to what



extent there exists agreement between theory and experiment. The dielectric constant of He, measured at 0°C and 1 atmosphere, is found experimentally to be  $\epsilon_r = 1.0000684$ ; under these conditions, the gas contains approximately  $N = 2.7 \times 10^{25}$  atoms per m<sup>3</sup>. For the model used above we find from (2.12) and (2.14)

$$\epsilon_r - 1 = 4\pi NR^3 \quad (2.15)$$

Calculating  $R$  from this expression and the numerical values of  $\epsilon_r$  and  $N$ , one obtains  $R \cong 0.6 \times 10^{-10}$  meter, which is indeed the correct order of magnitude for the radius of an atom. Thus, even though the model is rather crude, the results indicate that the interpretation is essentially correct. By way of illustration we give here the polarizability  $\alpha_s$  of rare gas atoms in  $10^{-40}$  farad m<sup>2</sup> as units.

	He	Ne	A	Kr	Xe
$\alpha_s \dots$	0.18	0.35	1.43	2.18	3.54

Note that the polarizability increases as the atoms become larger, in agreement with the results obtained for the model.

Let us now estimate the order of magnitude of the relative shift  $x$  of the nucleus and the center of the electron cloud, because this is the quantity which, together with the number of atoms per unit volume, determines  $\epsilon_r$ . For a field of, say,  $10^5$  volts per meter we obtain from (2.11) with  $R \approx 10^{-10}$  m and  $Z \approx 10$ ,  $x \cong 7 \times 10^{-18}$  m, which is very small indeed compared to the radius of the atom. The perturbing influence of an applied field on an atom is apparently very slight.

We note that the electronic polarizability of an atom is determined completely by its electronic structure; as long as the structure remains the same,  $\alpha_s$  remains the same. This notion is important because the electron structure of an atom is essentially independent of temperature, unless the temperature is extremely high. Thus, for normal temperatures,  $\alpha_s$  is *independent of temperature*. Consequently, if the number of atoms per unit volume is kept constant, the dielectric constant will also be independent of temperature. This is indeed what has been found experimentally for the rare gases. If the number of atoms per unit volume is allowed to change, the dielectric constant is simply proportional to this number.

## 2.4 Qualitative remarks on the dielectric constant of polyatomic molecules

The dielectric constant of polyatomic gases depends in many cases on temperature even if the number of molecules per m<sup>3</sup> is kept constant; in

other cases it may be constant. Some examples are given in Fig. 2.6 and in this section we shall deal with the physical interpretation of these ob-

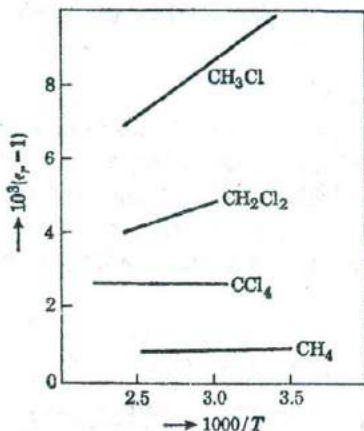


Fig. 2.6. The relative dielectric constant as a function of temperature ( $^{\circ}\text{K}$ ) for some gases at a pressure of 1 atmosphere.

servations. First of all, it should be realized that if two different atoms A and B form a chemical bond, one of the two is more apt to part with one or more of its valence electrons than the other. Thus, when  $Z_A e$  and  $Z_B e$  represent the nuclear charges of the two atoms, and if atom A has the tendency to give valence electrons to B, one finds on the average more than  $Z_B$  electrons around the nucleus B and fewer than  $Z_A$  electrons around the nucleus A. One says that atom A is more *electropositive* than B. Consequently, the bond between A and B is at least partly ionic (it is not necessary that A parts with an integral number of electrons; an electron may spend more time near B than near A, so that on the average, A has parted only with a fraction of the electron). If the bond between A and B has ionic character, it is evident that the molecule AB carries an *electric dipole moment even in the absence of an applied field*. For obvious reasons, such a dipole moment is called *permanent*, and will be denoted by the vector  $\mu_p$ . The magnitude of the dipole moment is given by the product of the average charge transferred from A to B and the internuclear distance. For a molecule consisting of more than two atoms, several bonds may carry a permanent dipole moment and the resulting permanent dipole moment of the molecule as a whole is obtained by vector addition of the moments associated with the various bonds. This is illustrated in Fig. 2.7 for two hypothetical cases corresponding to the type ABA. It is observed that the resultant dipole moment may be zero, viz. if the molecule has a center of symmetry.



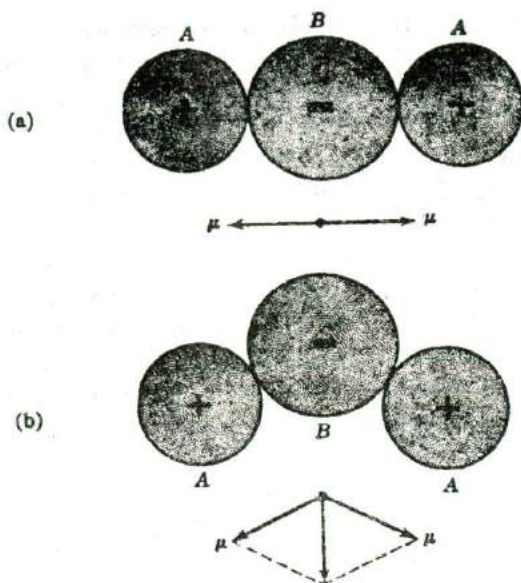


Fig. 2.7. Two possible configurations of a molecule  $A_2B$ . In (a) the resultant dipole moment is zero; in (b) there is a resultant dipole moment given by the vector sum of the dipole moments of the individual ionic bonds.

It will be evident that molecules such as  $O_2$ ,  $H_2$ ,  $N_2$  etc., which consist of similar atoms, carry no permanent dipole moment.

When an external field  $\mathbf{E}$  is applied to a molecule carrying a permanent dipole moment  $\mu_p$ , the external field will tend to align  $\mu_p$  along the direction of  $\mathbf{E}$ , since  $\mathbf{E}$  exerts a torque on  $\mu_p$ . The contribution of this process of orientation of the permanent dipoles to the polarization  $\mathbf{P}$  is called *orientational polarization*, and will be denoted by  $\mathbf{P}_o$ . Furthermore, the effect of an external field will be to shift the electron clouds in the molecule relative to the respective nuclei. In a molecular gas, therefore, we also have *electronic polarization*, as in a monoatomic gas, the only difference being that the molecules consist of more than one atom. In analogy with the electronic polarizability of a single atom, one defines the *electronic polarizability of a molecule* as the dipole moment induced per unit field strength resulting only from shifts of the electron clouds relative to the nuclei, i.e.

$$\mu_{\text{ind}} = \alpha_e \mathbf{E} \quad (2.16)$$

It is understood that this induced dipole moment represents an average value, the average being taken over all possible orientations of the molecule

relative to the field; this stipulation is necessary because the induced dipole moment of a molecule such as AB evidently depends on the angle between the direction of  $\mathbf{E}$  and the line joining the nuclei of the molecule.

Besides the two contributions to the polarization of a molecular gas just mentioned, there is a third contribution which is referred to as the *ionic polarization*. This contribution takes account of the fact that when in a molecule some of the atoms have an excess positive or negative charge (resulting from the ionic character of the bonds), an electric field will tend to shift positive ions relative to negative ones. This leads to an induced moment of different origin from the moment induced by electronic clouds shifting relative to nuclei. The difference between ionic and electronic polarization may be illustrated with reference to the string of ions represented in Fig. 2.8. The electronic polarizability measures the shift of

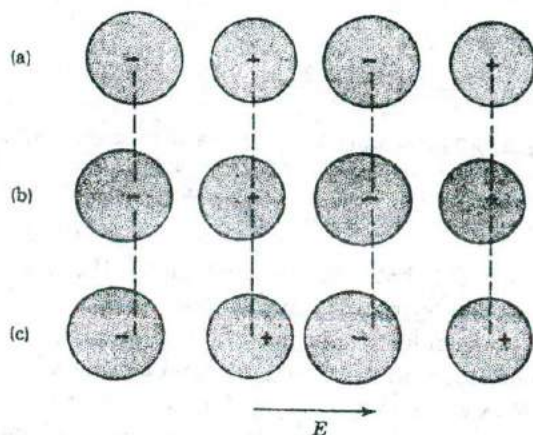


Fig. 2.8. A string of positive and negative ions is represented in (a) in the absence of a field. In (b) all electron clouds are shifted to the left as a result of the field, but the nuclei have been fixed; this corresponds to electronic polarization. In (c) the polarized ions are displaced relative to each other; the positive ions to the right, the negative ions to the left. In (c) therefore there is electronic as well as ionic polarization.

the electron clouds in the ions relative to the nuclei to which they belong. The ionic polarizability measures the shift of the ions relative to each other. A molecule may thus be characterized by an ionic polarizability  $\alpha_i$  defined in a way similar to  $\alpha_e$ .

Summarizing this section, we can distinguish between the following contributions to the polarization in a polyatomic gas:



- (i) the *orientational polarization* ( $P_o$ );
- (ii) the *electronic polarization* ( $P_e$ );
- (iii) the *ionic polarization* ( $P_i$ ).

The total polarization is given by the sum of these three quantities.

## 2.5 Quantitative discussion of the dielectric constant of polyatomic gases

Consider a gas containing  $N$  molecules per  $\text{m}^3$ . We shall assume the molecules carry a permanent electric dipole moment  $\mu_p$ ; the electronic and ionic polarizabilities of the molecules will be denoted respectively by  $\alpha_e$  and  $\alpha_i$ . The questions we shall answer in this section are these: What is the relationship between the dielectric constant  $\epsilon_r$  and the atomic quantities given? Does this relationship agree with experimental information of particular gases, and if so, what can one learn from such information?

From what has been said in the preceding section, we can write down the electronic and ionic contributions to the total polarization immediately as

$$P_e + P_i = N(\alpha_e + \alpha_i)E \quad (2.17)$$

where  $E$  is the applied field. We mentioned before that  $\alpha_e$  is independent of the temperature  $T$  as long as the electronic structure of the molecule remains unaltered. By the same token,  $\alpha_i$  will be independent of temperature if the electronic structure does not change. We thus conclude that for the usual temperatures of interest,  $(\alpha_e + \alpha_i)$  may be considered independent of  $T$ .

A calculation of the orientational polarization  $P_o$  is somewhat more complicated; we shall see that  $P_o$  does depend on temperature. Consider a system of  $N$  permanent dipoles of magnitude  $\mu_p$  in the absence of a field; let the temperature be  $T$ . Since there is no preference for any particular direction, the vector sum of all the individual  $\mu_p$ 's will vanish; i.e., there is no polarization in the absence of a field. Suppose we choose an arbitrary direction and call this the  $x$ -axis. The number of molecules  $N(\theta) d\theta$  for which the direction of  $\mu_p$  at a given instant lies within an angle between  $\theta$  and  $(\theta + d\theta)$  with the  $x$ -axis is then simply proportional to the solid angle  $2\pi \sin \theta d\theta$ , as indicated in Fig. 2.9. Suppose now, a field  $\mathbf{E}$  is applied along the  $x$ -direction. The number of molecules for which the direction of  $\mu_p$  at a given instant now lies within an angle between  $\theta$  and  $(\theta + d\theta)$  with the  $x$ -axis is no longer proportional to  $2\pi \sin \theta d\theta$ , for the

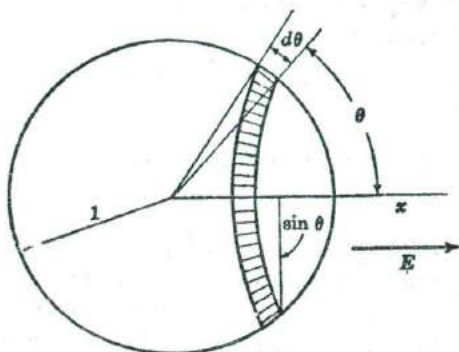


Fig. 2.9. Illustrating the geometry used in calculating  $N(\theta) d\theta$ . The area of the shaded ring between  $\theta$  and  $\theta + d\theta$  is equal to  $2\pi \sin \theta d\theta$ .

simple reason that the field  $E$  makes the  $x$ -axis a preferred direction; we shall show in fact, that the number is given by

$$N(\theta) d\theta = A2\pi \sin \theta d\theta \exp [(\mu_p E \cos \theta)/kT] \quad (2.18)$$

where  $k$  is Boltzmann's constant ( $= 1.38 \times 10^{-23}$  joule per-degree C), and  $A$  is a constant of proportionality determined by the total number of dipoles  $N$  under consideration. To derive (2.18), first consider the energy of a dipole  $\mu_p$  in the external field  $E$ . As indicated in Fig. 2.10, the torque

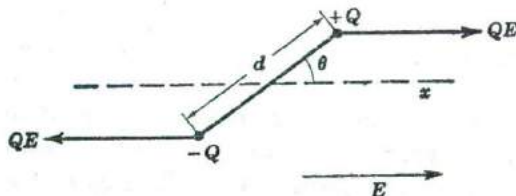


Fig. 2.10. Illustrating the forces exerted by a field  $E$  on the two charges of a dipole. The torque produced is equal to  $QEd \sin \theta = \mu_p E \sin \theta$ .

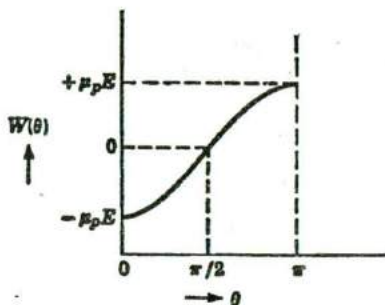
produced by the field on  $\mu_p$  is equal to  $\mu_p E \sin \theta$ . Let us arbitrarily set the energy of a dipole in the field equal to zero if  $\theta = 90$  deg. The energy  $W(\theta)$  of the dipole for an arbitrary angle  $\theta$  is then given by

$$W(\theta) = \int_{\theta=90^\circ}^{\theta} \mu_p E \sin \theta d\theta = -\mu_p E \cos \theta = -\mu_p \cdot E \quad (2.19)$$

From Fig. 2.11 we see that the energy is lowest for a dipole  $\mu_p$  parallel to  $E$ , and highest for a dipole antiparallel to  $E$ . In other words, *small angles  $\theta$  are preferred over large ones*. In fact, if there were no thermal motion,



Fig. 2.11. The potential energy of a dipole  $\mu_p$  as a function of the angle  $\theta$  between the dipole vector and an applied field.



all dipoles would line up along the external field direction. The reader who is familiar with the elements of Boltzmann statistics will now recognize that the population corresponding to a solid angle  $2\pi \sin \theta d\theta$  must be weighted by a Boltzmann factor  $\exp[-W(\theta)/kT]$  so that (2.18) follows immediately from this and (2.19).

Our next task is to find an expression for  $P_o$  on the basis of our result (2.18). It will be evident that  $P_o$  is parallel to  $\mathbf{E}$ ; i.e., we are interested in finding the sum of the *components* of the individual  $\mu_p$  along the direction of  $\mathbf{E}$ . Since a dipole  $\mu_p$  which makes an angle  $\theta$  with  $\mathbf{E}$  has a component along  $\mathbf{E}$  equal to  $\mu_p \cos \theta$ , one may write

$$P_o = \int_{\theta=0}^{\pi} N(\theta) d\theta \mu_p \cos \theta \quad (2.20)$$

Substituting (2.18) into (2.20) and making use of the fact that  $N = \int_0^{\pi} N(\theta) d\theta$ , the constant  $2\pi A$  may be eliminated and one obtains

$$P_o = N \frac{\int_0^{\pi} \mu_p \cos \theta \exp [(\mu_p E \cos \theta)/kT] \sin \theta d\theta}{\int_0^{\pi} \exp [(\mu_p E \cos \theta)/kT] \sin \theta d\theta} \quad (2.21)$$

Introducing the new variable  $y = (\mu_p E \cos \theta)/kT$  and writing for convenience  $\mu_p E/kT = a$ , the reader may verify that this leads to

$$P_o = (NkT/E) \frac{\int_{-a}^{+a} y e^y dy}{\int_{-a}^{+a} e^y dy} = N\mu_p \left[ \coth a - \frac{1}{a} \right] \equiv N\mu_p L(a) \quad (2.22)$$

The function  $L(a)$  defined by (2.22) is called the *Langevin function*; it first appeared in a study by Langevin (1905) of the similar problem of orientation of magnetic dipoles in a magnetic field. The function  $L(a)$  is represented in Fig. 2.12. For large values of  $a$  it approaches unity and hence  $P_o$  approaches  $N\mu_p$ . Physically, this corresponds to the situation in which  $\mu_p E/kT$  is so large that one approaches complete alignment of

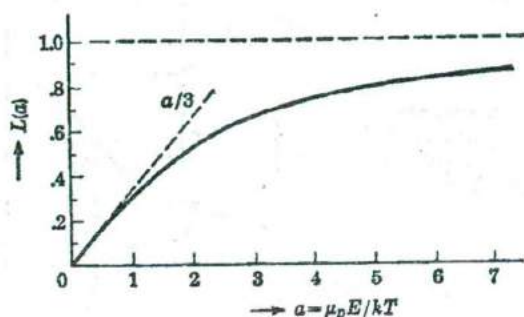


Fig. 2.12. The Langevin function  $L(a)$ ; for  $a \ll 1$ ,  $L(a) \cong a/3$ .

the dipoles along the field direction. In practice, this approach to saturation of the orientational polarization is never encountered in the case of gases; in fact, for practical purposes we may assume  $a = \mu_p E / kT \ll 1$ . This can be seen as follows: the magnitude of a permanent dipole moment may be anticipated to be of the order of the product of an electronic charge and one angstrom. It is for this reason that electric dipole moments are usually expressed in so-called debye units:

$$1 \text{ debye unit} = 10^{-18} \text{ esu angstrom} = 3.33 \times 10^{-30} \text{ coulomb meter}$$

Debye postulated the existence of permanent dipoles in molecules in 1912 and has contributed a great deal to our present understanding of dielectrics. Assuming for the moment permanent dipole moments of 1 debye unit, one finds even for a strong field of  $10^7$  volts per meter at room temperature,  $a \approx 0.01$ , which is small compared to 1. Under these circumstances expression (2.22) simplifies to

$$P_o = N\mu_p^2 E / 3kT \quad (2.23)$$

Thus, the orientational polarization is inversely proportional to the temperature and proportional to the square of the permanent dipole moment. Note that the slope of the Langevin function for small values of  $a$  is  $\frac{1}{3}$ . Also note that this derivation shows clearly that the tendency of the external field to align the dipoles is counteracted by the thermal motion, resulting in a decreasing value of  $P_o$  with increasing  $T$ .

The total polarization of a polyatomic gas is given by the sum of (2.17) and (2.23), i.e.

$$P = N(\alpha_e + \alpha_i + \mu_p^2 / 3kT)E \quad (2.24)$$

Comparing this with the general relation (2.9) from the macroscopic theory, we find that the dielectric constant  $\epsilon_r$  is related to the molecular

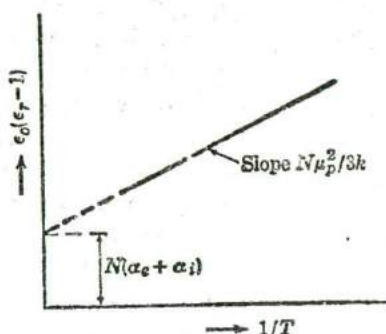


properties as follows:

$$\epsilon_0(\epsilon_r - 1) = N(\alpha_e + \alpha_i + \mu_p^2/3kT) \quad (2.25)$$

Let us now turn to the question of how this result can be compared with experimental information. It is observed that if the dielectric constant  $\epsilon_r$  is plotted as a function of  $1/T$ , expression (2.25) predicts the result to be a straight line. The slope of this line is determined by  $\mu_p^2$ ; the intercept with the axis  $1/T = 0$  provides a measure for  $\alpha_e + \alpha_i$ . In Fig. 2.6 we showed some experimental results which indeed confirm the temperature dependence predicted by (2.25). From such measurements one can evidently calculate the permanent dipole moment of the molecules as well

Fig. 2.13. Illustrating the relationship between  $\epsilon_r$  and  $1/T$  as predicted by expression (2.25). From the slope one can determine the permanent dipole moment of the molecules, and from the intercept of the ordinate, obtained by extrapolation, the sum  $(\alpha_e + \alpha_i)$  may be found.



as the sum  $\alpha_e + \alpha_i$ , provided the number of molecules per  $m^3$  is known, as indicated in Fig. 2.13. By way of illustration, we give in Table 2.1 some permanent dipole moment in debye units obtained from measurements of the dielectric constant in the gas phase. From the results obtained,

**Table 2.1.** EXPERIMENTALLY DETERMINED PERMANENT DIPOLE MOMENTS OF VARIOUS MOLECULES (IN DEBYE UNITS,  $3.33 \times 10^{-30}$  COULOMB METER)

Molecule	$\mu_p$	Molecule	$\mu_p$
NO	0.1	CO <sub>2</sub>	0
CO	0.11	CS <sub>2</sub>	0
HCl	1.04	H <sub>2</sub> O	1.84
HBr	0.79	H <sub>2</sub> S	0.93
HI	0.38	CH <sub>4</sub>	0
NO <sub>2</sub>	0.4	CH <sub>2</sub> Cl	1.15

one may derive certain conclusions with regard to the structure of the molecules. For example, the fact that CO<sub>2</sub> has no resultant dipole moment, whereas each of the CO bonds does have a dipole moment, indicates that in this molecule the two bonds make an angle of 180 degrees with each

other; the  $\text{CO}_2$  molecule thus must look like this:  $\text{O}=\text{C}=\text{O}$ . On the other hand, a molecule such as  $\text{H}_2\text{O}$  does have a resultant  $\mu_p$ , which indicates that the two OH bonds make an angle different from 180 degrees, and that the molecule has a triangular form (see Fig. 2.7). Dielectric constant measurements have been used a great deal as a tool for investigating molecular structure, but this subject lies outside the scope of the present text.

## 2.6 The internal field in solids and liquids

A detailed interpretation of the dielectric properties of solids and liquids is considerably more complicated than for gases, but a semi-quantitative understanding may be achieved on the basis of the concepts developed in the preceding sections. The main problem which arises in the case of solids and liquids is the calculation of what is known as the *local* or *internal field*  $\mathbf{E}_i$ , which is defined as the field acting at the location of a given atom. In the case of a gas, we assumed that the internal field was equal to the applied field  $\mathbf{E}$ , and as long as the density of molecules is reasonably low, this is a good approximation. However, in solids and liquids the molecules or atoms are so close together that the field seen by a given particle is determined in part by the dipoles carried by surrounding particles; in general, therefore,  $\mathbf{E}_i$  is not equal to the applied field  $\mathbf{E}$ .

To illustrate this for a simple example, consider an infinite string of similar equidistant atoms of polarizability  $\alpha$ , as indicated in Fig. 2.14.\*

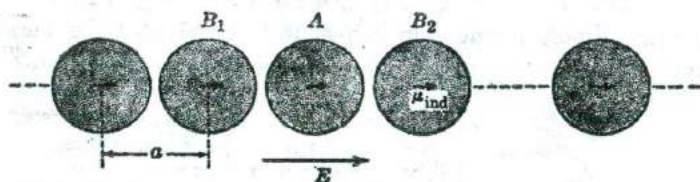


Fig. 2.14. Illustrating a string of atoms of polarizability  $\alpha$ , in an external field parallel to the string. The induced dipole moments are indicated.

Given an external field  $\mathbf{E}$  applied in a direction parallel to the string, what is the internal field at the position of a given atom? With reference to Fig. 2.14 let the field seen by atom A be  $\mathbf{E}_i$ ; from the symmetry of the problem it is evident that  $\mathbf{E}_i$  will be parallel to  $\mathbf{E}$  and furthermore, in the

\* The author noticed this particular model in the present context for the first time in a set of lecture notes of Professor D. J. Epstein (M.I.T.), who kindly gave his permission to include it in this book.



example chosen, the field seen by the other atoms will be the same. The dipole moment induced in each of the atoms of the string is thus

$$\mu_{\text{ind}} = \alpha_e \mathbf{E}_i \quad (2.26)$$

and our problem is to evaluate  $\mathbf{E}_i$ . Clearly,  $\mathbf{E}_i$  must be equal to the applied field  $\mathbf{E}$  plus the field produced at the location of A by the dipoles on all other atoms. Let us proceed to calculate the field produced at the center of A by the dipole on atom  $B_1$  in Fig. 2.14; we shall assume that the dipoles may be considered as point dipoles. According to field theory, the potential around a point dipole  $\mu$  in vacuum is given by

$$V(r, \theta) = \frac{1}{4\pi\epsilon_0} \frac{\mu \cos \theta}{r^2} \quad (2.27)$$

where  $r$  is the distance from the dipole and  $\theta$  is the angle between  $\mathbf{r}$  and  $\mu$ . The field around a dipole, therefore, has two components given by

$$E_r = -\frac{\partial V}{\partial r} = \frac{1}{4\pi\epsilon_0} \frac{2\mu \cos \theta}{r^3} \quad (2.28)$$

and

$$E_\theta = -\frac{1}{r} \frac{\partial V}{\partial \theta} = \frac{1}{4\pi\epsilon_0} \frac{\mu \sin \theta}{r^3} \quad (2.29)$$

These components are indicated in Fig. 2.15. Thus, the field produced by  $B_1$  at the location of atom A is obtained from the last two expressions by

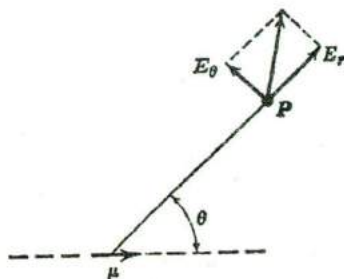


Fig. 2.15. Illustrating the field components  $E_r$  and  $E_\theta$  in a point  $P$  resulting from a dipole  $\mu$ .

putting  $r = a$  and  $\theta = 0$ ; this gives a contribution of  $\mu_{\text{ind}}/2\pi\epsilon_0 a^3$  in the direction of  $\mathbf{E}$ . It is readily verified that the field produced at A by the dipole on  $B_2$  is equal to that produced by  $B_1$ . Following the same procedure for the other atoms in the string, we find for the internal field at A

$$\mathbf{E}_i = \mathbf{E} + \left( \frac{\mu_{\text{ind}}}{\pi\epsilon_0 a^3} \right) \sum_{n=1}^{\infty} \frac{1}{n^3} \quad (2.30)$$

where  $n$  accepts the integer values 1, 2, 3 . . . . Substituting  $\mu_{\text{ind}}$  from

(2.26) into (2.30) we can express  $E_i$  in terms of the applied field  $E$ . The sum in (2.30) is approximately equal to 1.2, and we obtain

$$E_i = \frac{E}{1 - 1.2\alpha_e/\pi\epsilon_0 a^3} = \frac{E}{1 - \beta} \quad (2.31)$$

Since the constant  $\beta$  is positive, we conclude that the *actual field seen by an atom in the string is larger than the applied field  $E$* . Physically this means that for the model chosen here, the dipoles *cooperate* with each other in the sense that a large dipole moment on a given atom helps induce a dipole moment in its neighbors, which in turn induce a dipole moment in the former, etc. It is observed<sub>2</sub> that the *cooperation becomes stronger as the polarizability of the atoms increases and as the distance between them decreases*. It is also observed that the internal field is determined in general by the *structure* of a given material, i.e. by the surroundings seen at the position of a given atom. An accurate calculation of the internal field in solids and liquids is in general very complicated and for our purposes it may be sufficient to point out a general feature of the relation between the internal and applied fields. We note that the last term in (2.30) is proportional to the dipole moment induced in the atoms. It is not surprising therefore that calculations of  $E_i$  in a three-dimensional case always give results which may be written in the form

$$E_i = E + (\gamma/\epsilon_0)P \quad (2.32)$$

where  $P$  is the dipole moment per unit volume and where  $\gamma$  is a proportionality constant which is referred to as the *internal field constant*;  $\epsilon_0$  has been introduced in (2.32) only for the purpose of making  $\gamma$  a dimensionless quantity. In general, the numerical value of  $\gamma$  is of the order of unity; for the linear chain of Fig. 2.14, for example, it follows immediately from (2.30) that  $\gamma = 1.2/\pi$ . A particular case which one encounters frequently in the literature on dielectrics is that corresponding to  $\gamma = \frac{1}{3}$ . One speaks in that case of the *Lorentz field*, given by

$$E_{i \text{ Lorentz}} = E + P/3\epsilon_0 \quad (2.33)$$

A derivation of this expression may be found in the references given at the end of this chapter; it holds only in particular cases, as when the atoms in a solid are surrounded cubically by other atoms. One should, therefore, be careful in applying the specific value  $\gamma = \frac{1}{3}$ , unless the particular symmetry conditions are met for which it has been derived. A further warning should be given here pertaining to the interpretation of the dielectric constant of liquids in which the molecules carry permanent dipoles (*polar liquids*). The internal field as it tends to orient the dipoles along



the direction of the external field is generally *different* from the internal field as it is used to calculate the contribution to the polarization resulting from  $\alpha_e$  and  $\alpha_i$ . At first sight, this may seem strange; in fact, this difference was not realized until it was pointed out by Onsager in 1936. In the material before that time, this oversight had resulted in erroneous interpretations of the dielectric behavior of polar liquids. For a discussion of the internal field in liquids we refer the reader to Bottcher's book.

## 2.7 The static dielectric constant of solids

In this section the general features of the dielectric behavior of solids will be discussed; for data concerning specific materials the reader is referred to *Dielectric Materials and Applications*, edited by von Hippel. The special behavior of ferroelectric and piezoelectric materials is dealt with in subsequent sections.

It is convenient to distinguish between three groups of solids in connection with their dielectric behavior:

(i) **Elemental dielectrics.** These are materials built up from only one kind of atoms, such as diamond, phosphorus, etc. It will be evident that in such materials there are no permanent dipoles or ions, so that the only contribution to the polarization is that due to the relative displacement of electron clouds and nuclei. Hence, for these materials  $P = P_e$  and  $P_i = P_o = 0$ . Denoting the electronic polarizability per atom by  $\alpha_e$ , we may write

$$P = N\alpha_e E_i \quad (2.34)$$

where  $E_i$  is the internal field and  $N$  represents the number of atoms per  $\text{m}^3$ . In writing expression (2.34) it has been assumed that the internal field is the same for all atoms. Since  $E_i$  is generally given by an expression like (2.32), we may write

$$P = N\alpha_e [E + (\gamma/\epsilon_0)P] \quad (2.35)$$

from which we can find  $P$  in terms of the applied field  $E$  as

$$P = \frac{N\alpha_e E}{1 - (\gamma N\alpha_e/\epsilon_0)} \quad (2.36)$$

In order to obtain an expression for the dielectric constant  $\epsilon_r$  in terms of the atomic quantities we turn to the macroscopic expression (2.9); from it and (2.36) we then find

$$\epsilon_0(\epsilon_r - 1) = \frac{N\alpha_e}{1 - \gamma N\alpha_e/\epsilon_0} \quad (2.37)$$

In case we assume  $\gamma = \frac{1}{3}$  (see preceding section), the same procedure leads to the so-called Clausius-Mosotti expression

$$\frac{\epsilon_r - 1}{\epsilon_r + 2} = \frac{N\alpha_e}{3\epsilon_0} \quad (2.38)$$

The dielectric constant is thus determined by  $N$ ,  $\alpha_e$  and  $\gamma$ . It should be noted that in general,  $\alpha_e$  is not the same as the polarizability of the free atoms, because the binding between the atoms affects the valence electrons; however, the two values may be nearly the same. The distance between the atoms in a solid is affected only slightly by temperature, and therefore  $N$ ,  $\alpha_e$ ,  $\gamma$ , and the dielectric constant  $\epsilon_r$  are in first approximation independent of temperature for the materials under discussion. By way of illustration we give here the dielectric constant  $\epsilon_r$  for three elements in the fourth group of the periodic table, all three having the diamond structure.

	Diamond	Si	Ge
$\epsilon_r \dots$	5.68	12	16

Although silicon and germanium are poor insulators, one can still speak of a dielectric constant for such materials. It may be worthwhile to point out that  $(\epsilon_r - 1)$  for these and for most other solids is of the order of unity or ten, whereas for gases at normal temperature and pressure the same quantity is of the order of  $10^{-3}$  or  $10^{-4}$ . This difference of course reflects the difference in the number of atoms per unit volume, as may be seen from (2.37). In fact, a representative figure for the number of atoms per  $m^3$  in a solid or liquid is  $N \cong 5 \times 10^{28} m^{-3}$ . Accurate values in specific cases may be obtained from X-ray diffraction data; such data provide information about the crystal structure and the interatomic distances.

(ii) **Ionic dielectrics without permanent dipoles.** In ionic crystals such as the alkali halides, the total polarization is made up of electronic and ionic polarization, i.e.

$$P = P_e + P_i \quad (2.39)$$

A crystal of this kind, when considered as a huge molecule, has no permanent electric dipole moment, because the sum

$$\mu_p = \sum_i e_i x_i$$

(see section 2.2) vanishes; hence,  $P_o = 0$ . The dielectric behavior of such materials is more complicated than that of group (i) from the point of view of quantitative interpretation; the internal field at the positive ion sites, for example, is in general different from that at the negative ion sites.



Without going into details with reference to the interpretation, it may be of interest to point out that the ionic polarization  $P_i$  usually constitutes a considerable fraction of the total polarization. Experimentally this has been established as follows: when one measures the dielectric constant at frequencies of approximately  $5 \times 10^{14} \text{ sec}^{-1}$ , corresponding to the visible part of the electromagnetic spectrum, the relatively heavy positive and negative ions can no longer follow the rapid field variations. Consequently, one measures in that region only the electronic polarization  $P_e$ . Since a measurement of the static dielectric constant gives  $P_e + P_i$ , it is thus possible to find  $P_e$  and  $P_i$  separately. Quantitatively this may be expressed in the following manner: Let  $\epsilon_{rs}$  represent the static value of the relative dielectric constant; we may then write in accordance with (2.9)

$$\epsilon_0(\epsilon_{rs} - 1)E = P_e + P_i \quad (2.40)$$

Similarly, when  $\epsilon_{re}$  represents the dielectric constant measured at optical frequencies, one may write

$$\epsilon_0(\epsilon_{re} - 1)E = P_e \quad (2.41)$$

From these expressions it is obvious that the *difference between  $\epsilon_{rs}$  and  $\epsilon_{re}$  is a measure for the ionic polarization*. The values of  $\epsilon_{rs}$  and  $\epsilon_{re}$  given in Table 2.2 for alkali halides illustrate clearly that the static dielectric con-

**Table 2.2.** STATIC AND OPTICAL DIELECTRIC CONSTANTS,  $\epsilon_{rs}$  AND  $\epsilon_{re}$ , FOR ALKALI HALIDES;  $n$  REPRESENTS THE INDEX OF REFRACTION

Solid	$\epsilon_{rs}$	$\epsilon_{re} = n^2$	Solid	$\epsilon_{rs}$	$\epsilon_{re} = n^2$
LiF	9.27	1.92	KF	6.05	1.85
LiCl	11.05	2.75	KCl	4.68	2.13
LiBr	12.1	3.16	KBr	4.78	2.33
LiI	11.03	3.80	KI	4.94	2.69
NaF	6.0	1.74	RbF	5.91	1.93
NaCl	5.62	2.25	RbCl	5.0	2.19
NaBr	5.99	2.62	RbBr	5.0	2.33
NaI	6.60	2.91	RbI	5.0	2.63

stant of these materials contains an appreciable contribution from the displacement of the positive ion lattice relative to the negative ion lattice in an external field. It should be mentioned here that in the optical region of the electromagnetic spectrum, one measures the dielectric constant by determining the *index of refraction  $n$* . According to Maxwell's theory of electromagnetic waves,  $\epsilon_{re} = n^2$  for materials with a magnetic permeability equal to that of vacuum.

It may be of interest to point out that there exists a relationship be-

tween the difference ( $\epsilon_{rs} - \epsilon_{rl}$ ) and the compressibility of these materials. This may be seen as follows: The compressibility of a material is defined as the fractional change in volume per unit change in pressure. It is evident that the compressibility of a material will be small for "hard" atoms and large for "soft" atoms. In the case of an ionic solid, the applied field tends to shift the positive ion lattice in a direction opposite to that in which the negative ions tend to move, so that for a system of "hard" ions, the ionic polarization per unit applied field will be smaller than for a system of "soft" ions. Thus, in general one expects large values of ( $\epsilon_{rs} - \epsilon_{rl}$ ) to be accompanied by large values of the mechanical compressibility of the material; this notion is in agreement with experimental evidence.

(iii) **Solids containing permanent dipole moments.** The molecules in many solids carry permanent electric dipole moments; solid nitrobenzene ( $C_6H_5NO_2$ ) is an example of this group. The dielectric constant in the vicinity of the melting point of this material is represented in Fig. 2.16.

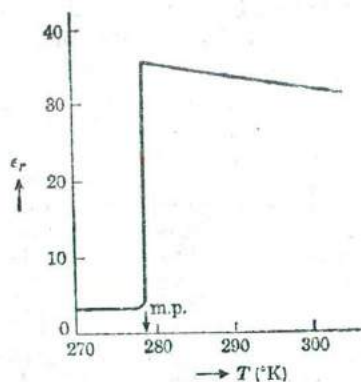


Fig. 2.16. Relative dielectric constant of nitrobenzene as a function of temperature in the vicinity of the melting point. [After C. P. Smyth and C. S. Hitchcock, *J. Am. Chem. Soc.*, **55**, 1296 (1933)]

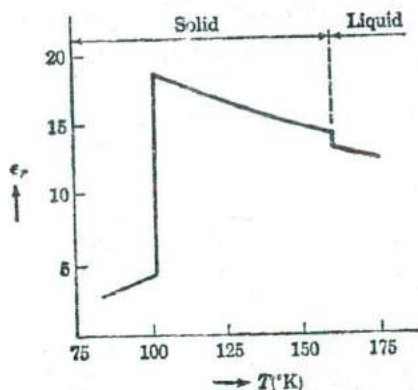


Fig. 2.17. The relative dielectric constant of solid and liquid HCl as a function of temperature. [After C. P. Smyth and C. S. Hitchcock, *J. Am. Chem. Soc.*, **55**, 1830 (1933)]

It is observed that as the material freezes, the dielectric constant  $\epsilon_r$  decreases abruptly from a value near 35 to a much lower value. It is also observed that in the solid state  $\epsilon_r$  is independent of temperature, whereas in the liquid state it decreases with increasing temperature. These observations can be understood qualitatively on the basis of the concepts



developed in the preceding sections. In the liquid state,  $\epsilon_r$  is determined by the electronic, ionic, and orientational contributions. The decrease of  $\epsilon_r$  with increasing temperature must evidently be ascribed to the fact that the orientational contribution decreases with temperature, as it does in the case of gases [see formula (2.25)]. The sudden drop in  $\epsilon_r$  at the melting point is interpreted as meaning that even though the solid contains permanent dipoles, these are "frozen" in the solid state and can no longer be aligned by an external field. Thus, in the solid state one only measures the contributions to  $\epsilon_r$  associated with electronic and ionic polarization. This also explains the fact that in the solid state the temperature dependence of  $\epsilon_r$  has disappeared.

In some solids, the permanent dipoles may still contribute to the polarization, although their motion may be strongly inhibited. An example is given in Fig. 2.17. It is observed that as HCl goes from the liquid state to the solid state at 159°K,  $\epsilon_r$  increases abruptly by a small amount; this is due to the change in density upon solidification. However, in the solid state,  $\epsilon_r$  keeps increasing with decreasing temperature, indicating the presence of orientational polarization. It is not until a temperature of 100°K has been reached that  $\epsilon_r$  drops sharply, a result of the fact that the dipoles have become immobile.

After what has been said concerning the static dielectric constant of solids, there is little to be added about the same quantity in the case of liquids. In general,  $\epsilon_r$  will decrease with increasing temperature as a result of a reduction in the orientational polarization. If there are no permanent dipoles present,  $\epsilon_r$  is nearly independent of temperature.

## 2.8 Some properties of ferroelectric materials

For the dielectric materials discussed in the preceding sections, the polarization is a linear function of the applied field. There are, however, a number of substances for which the polarization of a specimen depends on its history; i.e., the polarization in these materials is not a unique function of the field strength. In particular, these materials exhibit *hysteresis* effects, similar to those observed in ferromagnetic materials; they are therefore called *ferroelectric* materials. An example of a hysteresis loop associated with the polarization versus field strength is given in Fig. 2.18. When an electric field is applied to a "virgin" specimen of a ferroelectric material, the polarization increases along a curve such as *OABC* in Fig. 2.18. When the field is reduced, it is observed that for  $E = 0$ , a certain amount of *remanent polarization*,  $P_r$ , is still present. In other

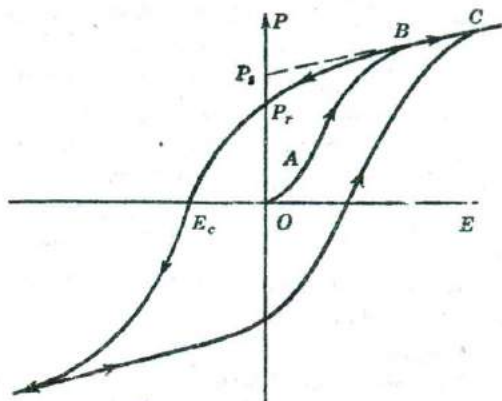


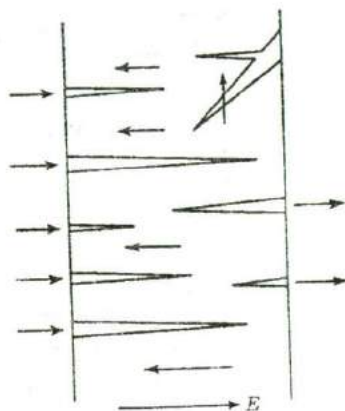
Fig. 2.18. Schematic representation of a hysteresis curve for a ferroelectric material.  $P_r$  represents the remanent polarization,  $P_s$  the spontaneous magnetization. The slope along  $BC$  is due to "normal" dielectric polarization.  $E_c$  is the coercive field.

words, the material is *spontaneously polarized*. In order to make the polarization equal to zero, a field in the opposite direction must be applied; this field is called the *coercive field*, and is denoted by  $E_c$  in Fig. 2.18.

The hysteresis loop may be explained qualitatively in the following manner: the direction of the spontaneous polarization is generally not the same throughout a macroscopic specimen. In fact, the specimen may be considered to consist of a number of *domains* which are themselves spontaneously polarized, but with the direction of polarization varying from one domain to another. Thus, a virgin macroscopic specimen may have zero polarization as a whole; i.e., the resultant of the polarization vectors of the individual domains may vanish. Upon application of an electric field, the domains for which the polarization points along the direction of the applied field grow at the expense of other domains for which the polarization points in other directions. This process corresponds to the curve  $OAB$  in Fig. 2.18. Ultimately, the specimen may have become one single domain, and the further slight increase of  $P$  with increasing applied field is due to "normal" polarization as discussed in preceding sections. The domain structure can be studied in ferroelectric materials, for example, by employing polarized light, which makes domains visible. In Fig. 2.19 we have illustrated schematically how the polarization of a crystal of  $\text{BaTiO}_3$  (barium titanate) may change direction under the influence of a field which has a direction opposite to that of the spontaneous polarization. Domains with a polarization parallel to the applied field evidently



Fig. 2.19. Schematic representation of new domains resulting from application of a field  $E$  directed oppositely to the spontaneous polarization of a specimen.



grow in the form of thin needles of approximately  $10^{-6}$  m width; these domains grow essentially in the *forward* direction until ultimately the polarization of the specimen lies along the applied field direction. This process is quite different from that encountered in ferromagnetism, as we shall see in Chapter 4.

The *spontaneous polarization*, which is the most characteristic property of a ferroelectric material, usually vanishes above a certain temperature  $\theta_f$ ; this temperature is called the ferroelectric *Curie temperature*. In the ferroelectric region, i.e. below  $\theta_f$ , the dielectric constant is evidently a function of the field strength and is no longer a "constant." One can, of course, define a differential relative dielectric constant defined on the basis of (2.9) by the equation

$$\epsilon_0(\epsilon_r - 1) = dP/dE \quad (2.42)$$

When one speaks of "the dielectric constant" in the ferroelectric region one usually means  $\epsilon_r$  defined by (2.42) along the virgin curve at the origin. The dielectric constant so defined may reach very high values in the vicinity of the ferroelectric Curie temperature, as may be seen from Fig. 2.20 for barium titanate ceramic.

Above the Curie temperature, the dielectric constant varies with temperature in accordance with the so-called Curie-Weiss law

$$\epsilon = C/(T - \theta) \quad (2.43)$$

where  $C$  is a constant and  $\theta$  is a characteristic temperature which is usually a few degrees smaller than the ferroelectric Curie temperature  $\theta_f$ .

*Classification of ferroelectric materials.* There are various groups of ferroelectric materials which may be classified on the basis of their chemical composition and structure.

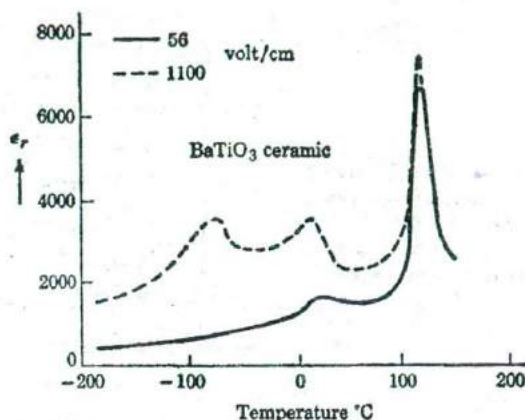


Fig. 2.20. Dielectric constant of barium titanate ceramic as a function of temperature. The fully drawn and the dashed curves correspond respectively to a peak field strength at 1 kc of 56 and 1100 volts per cm. The sharp peaks occur at the ferroelectric Curie temperature  $\theta_f$ . (After W. B. Westphal, Laboratory for Insulation Research, M.I.T.)

(i) The first solid which was recognized to exhibit ferroelectric properties is *Rochelle salt*, the sodium-potassium salt of tartaric acid ( $\text{NaKC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$ ). It has the peculiar property of being ferroelectric only in the temperature region between  $-18^{\circ}\text{C}$  and  $23^{\circ}\text{C}$ ; i.e., it has two transition temperatures. The spontaneous polarization of this material

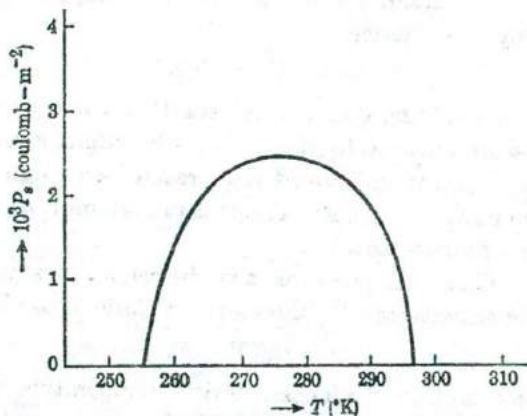


Fig. 2.21. Spontaneous polarization of Rochelle salt as a function of temperature. [After J. Halblützel, *Helv. Phys. Acta*, 12, 489 (1939)]



is represented in Fig. 2.21. Rochelle salt is representative of the *tartrate group* of ferroelectric materials; other members of this group are those in which a fraction of the potassium in Rochelle salt is replaced by  $\text{NH}_4$ , Rb or Tl.

(ii) In 1935 Busch and Scherrer discovered ferroelectric properties in  $\text{KH}_2\text{PO}_4$ , which is a typical example of the *dihydrogen phosphates* and *arsenates* of the alkali metals. The spontaneous polarization of this material is given in Fig. 2.22 as a function of temperature. The shape of this curve resembles that of the spontaneous magnetization in iron, as we shall see in Chapter 4. In this case, there is only one Curie temperature, viz.  $\theta_f = 123^\circ\text{K}$ .

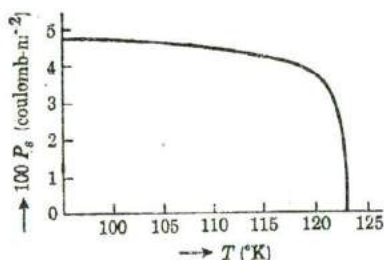


Fig. 2.22. Spontaneous polarization of  $\text{KH}_2\text{PO}_4$  as a function of temperature. [After A. von Arx and W. Bantle, *Helv. Phys. Acta*, 16, 221 (1943)]

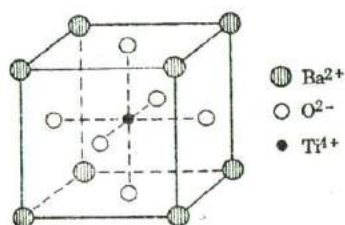


Fig. 2.23. The cubic structure of  $\text{BaTiO}_3$  above the ferroelectric Curie temperature.

(iii) Probably the best-known ferroelectric material is *barium titanate*  $\text{BaTiO}_3$ ; it is a representative of the so-called *oxygen octahedron group* of ferroelectric materials. The reason for this name is that above the Curie temperature ( $\theta = 120^\circ\text{C}$ ),  $\text{BaTiO}_3$  corresponds to the cubic structure presented in Fig. 2.23. In this structure, the  $\text{Ba}^{2+}$  ions occupy the corners of a cube; the centers of the cube faces are occupied by  $\text{O}^{2-}$  ions. The oxygen ions form an octahedron, at the center of which the small  $\text{Ti}^{4+}$  ion is located. The  $\text{Ti}^{4+}$  ion is considerably smaller than the space which is available inside the oxygen octahedron. It thus brings with it a *high ionic polarizability* for two reasons: (a) it has a charge of  $4e$  and, (b) it can be displaced over a relatively large distance. We shall see that this may be the explanation for the occurrence of spontaneous polarization in  $\text{BaTiO}_3$ .

There is an intimate relationship between the ferroelectric properties and the atomic arrangement in ferroelectric materials. Above  $120^\circ\text{C}$ ,  $\text{BaTiO}_3$  has the cubic structure indicated in Fig. 2.23. When the tempera-

ture is lowered through the critical temperature of  $120^{\circ}\text{C}$ , the material becomes spontaneously polarized and at the same time the structure changes. The direction of spontaneous polarization may lie along any of the cube edges, giving a total 6 possible directions for the spontaneous polarization. Along the direction of spontaneous polarization of a given domain, the material expands, whereas perpendicular to the polarization direction it contracts. Thus, the material is no longer cubic, but corresponds to a so-called tetragonal structure.  $\text{BaTiO}_3$  has two more transition temperatures: one at  $5^{\circ}\text{C}$ , where the spontaneous polarization changes its direction from one of the cube edges to a direction corresponding to a face diagonal in Fig. 2.22; and one at  $-80^{\circ}\text{C}$  where the spontaneous polarization changes from a direction corresponding to a face diagonal to one along a body diagonal. Associated with each of these ferroelectric transitions is a change in the crystal structure of the material. These three transition temperatures are reflected in the dielectric constant and in the spontaneous polarization of the material, as may be seen from Figs. 2.24

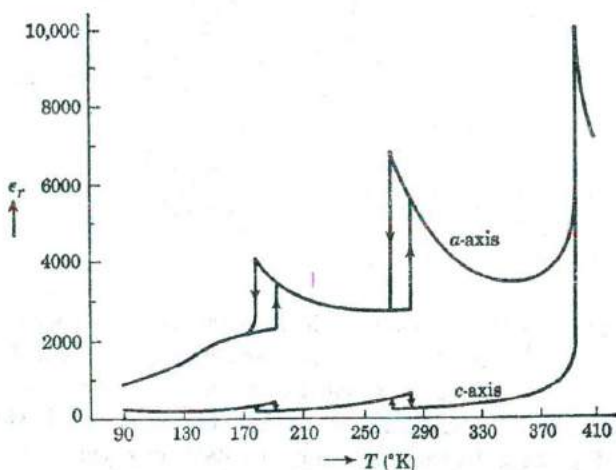


Fig. 2.24. The dielectric constant of  $\text{BaTiO}_3$  as a function of temperature. [After W. J. Merz, *Phys. Rev.* 76, 1221 (1949)]

and 2.25. The spontaneous polarization represented in Fig. 2.25 was measured along a cube edge over the whole temperature range. Thus, the magnitude in the region between  $193^{\circ}\text{K}$  and  $278^{\circ}\text{K}$  is obtained by multiplying the value given in Fig. 2.25 by  $\sqrt{2}$  ( $P$ , in that region is directed along a face diagonal!). Similarly, to obtain the magnitude of  $P$ , in the region below  $193^{\circ}\text{K}$ , one should multiply the value in Fig. 2.24 by  $\sqrt{3}$



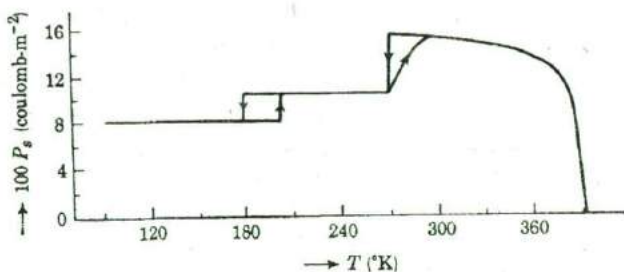


Fig. 2.25. The spontaneous polarization of BaTiO<sub>3</sub> measured along a cube edge. [After W. J. Merz, *Phys. Rev.* 76, 1221 (1949)]

( $P_s$  directed along body diagonal in this case!). Essentially, therefore, the magnitude of the spontaneous polarization below about 300°K is constant.

## 2.9 Spontaneous polarization

Although we do not intend to give here a detailed discussion of the theory of ferroelectricity, a few remarks should be made with reference to the occurrence of spontaneous polarization. In section 2.7 we noted that in normal solid dielectrics the internal field may be written in the form

$$E_i = E + (\gamma/\epsilon_0)P \quad (2.44)$$

where  $E$  is the applied field,  $P$  the polarization and  $\gamma$  the internal field constant. Although the internal field may be different for different atomic positions in the solid, for the sake of argument we shall assume (2.44) to be valid for all atoms in a hypothetical solid. Suppose this hypothetical solid can be built up by a three-dimensional stacking of units such as the cube in Fig. 2.23 in the case of BaTiO<sub>3</sub>. Let there be  $N$  of these units per m<sup>3</sup> and let the total polarizability per unit be  $\alpha$ . The polarization of the material may then be written as

$$P = N\alpha E_i = N\alpha[E + (\gamma/\epsilon_0)P] \quad (2.45)$$

from which we find upon solving for  $P$

$$P = \frac{N\alpha E}{1 - (N\alpha\gamma/\epsilon_0)} \quad (2.46)$$

Does this formula indicate the possibility of spontaneous polarization? What we are asking for is actually this: in the absence of an external field ( $E = 0$ ), does (2.46) allow a non-vanishing value for  $P$ ? The answer is, that such a solution indeed exists, viz. when the denominator in (2.46) equals zero. In other words, if  $N\alpha\gamma/\epsilon_0 = 1$ , spontaneous polarization is possible. Physically, this means that if the interaction between the atoms

is large enough (large  $\gamma$ ), and if  $N\alpha$  is large enough, spontaneous polarization may occur. We may also look at this from a somewhat different point of view. Consider the string of atoms in Fig. 2.18 in the absence of an external field. The string may then occur in two states: (i) the atoms are not polarized; i.e., they carry no dipoles; (ii) the atoms induce in each other dipoles such that the string is spontaneously polarized. Which of these two states is realized depends on the energy of the system in the two states. If the energy of the string in the spontaneously polarized state is lower than that of the unpolarized state, the spontaneously polarized state will be the stable configuration of the system; if the energy of the spontaneously polarized string is higher than that of the unpolarized string, the system will not be spontaneously polarized.

Still another way of looking at the condition for spontaneous polarization emerges by writing (2.46) in the form

$$\frac{P}{E} = \frac{N\alpha}{1 - (N\alpha\gamma/\epsilon_0)} = \frac{A}{1 - A\beta} \quad (2.47)$$

where  $\beta = \gamma/\epsilon_0$ . In this form, the last expression reminds us of the gain of an amplifier with an amplification  $A$  and a feedback factor  $\beta$  (see Fig. 2.26). If there were no feedback; i.e., if the internal field were the same as

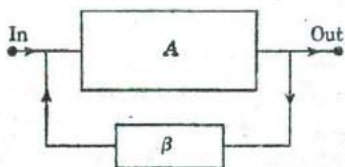


Fig. 2.26. Schematic representation of an amplifier with gain  $A$  and a feedback loop  $\beta$ . The total gain is given by expression (2.47).

the applied field, corresponding to  $\beta = \gamma = 0$ , the "gain" (which in this case corresponds to the polarization per unit field) would be simply  $N\alpha = A$ . As a result of the feedback associated with the internal field constant  $\gamma$ , the gain is in general larger than  $N\alpha$ , and may become infinite if  $A\beta = N\alpha\gamma/\epsilon_0 = 1$ .

It will be evident from the discussion that a high polarizability  $\alpha$  is one of the factors which is favorable for the occurrence of spontaneous polarization. In this connection we remind the reader of a remark made earlier in connection with the high ionic polarizability associated with the  $Ti^{4+}$  ion in  $BaTiO_3$ ; this is presumably one of the factors which give rise to the spontaneous polarization in this material.

The next question which arises is this: why does spontaneous polarization usually occur only below a certain temperature? We shall consider here one possible cause for the existence of a Curie temperature. Let



us start from equation (2.46), assuming that this expression applies in the nonferroelectric region ( $T \geq \theta_f$ ). From the general expression  $P = \epsilon_0(\epsilon_r - 1)E$  it then follows that the dielectric constant of the material satisfies the relation:

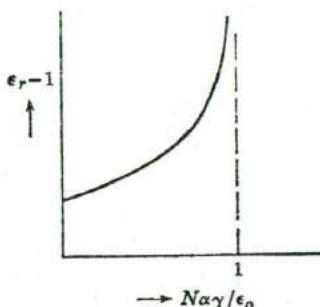
$$\epsilon_r - 1 = \frac{N\alpha/\epsilon_0}{1 - N\alpha\gamma/\epsilon_0} \quad (2.48)$$

Let us inquire about the temperature dependence of  $\epsilon_r$ , assuming for simplicity that  $\alpha$  and  $\gamma$  are temperature independent and that only  $N$  is a function of temperature. If  $\lambda$  represents the coefficient of volume expansion of the material, then we have evidently

$$\frac{1}{N} \frac{dN}{dT} = -\lambda \quad (2.49)$$

The minus sign indicates that as  $T$  increases the volume increases and hence  $N$  decreases. Now, in "normal" dielectrics for which  $\epsilon_r$  is of the order of unity or ten, the influence of expansion of the material with increasing temperature has very little influence on  $\epsilon_r$  if  $\alpha$  and  $\gamma$  are independent of  $T$ . However, we see from (2.48) that if at a certain temperature  $T_1$  the quantity  $N(T_1)\alpha\gamma/\epsilon_0$  is only slightly smaller than 1, cooling of the sample may increase  $N$  sufficiently to make  $N\alpha\gamma/\epsilon_0$  equal to 1 for some temperature  $\theta_f$  below  $T_1$ , with the result that spontaneous polarization may set in at  $T = \theta_f$ . At the same time,  $\epsilon_r - 1$  would be very large in the vicinity of the critical temperature (see Fig. 2.27). These qualitative arguments

Fig. 2.27. Schematic representation of  $\epsilon_r - 1$  as a function of  $N\alpha\gamma/\epsilon_0$ , according to formula (2.48). The value  $N\alpha\gamma/\epsilon_0 = 1$  corresponds to the ferroelectric Curie temperature;  $N\alpha\gamma/\epsilon_0 < 1$  corresponds to temperatures above the ferroelectric Curie temperature.



show that a Curie temperature may arise in a material of high  $\epsilon_r$ , simply as a result of the contraction of the material upon cooling.

Assuming the model is correct, how does  $\epsilon_r$  vary with temperature in the vicinity of the Curie temperature? Solving for  $N$  from (2.48) we find

$$N = \frac{\epsilon_0}{\alpha} \frac{\epsilon_r - 1}{(\epsilon_r - 1)\gamma + 1} \quad (2.50)$$

Differentiating both sides with respect to  $T$  and dividing through by  $N$  we obtain

$$\frac{1}{N} \frac{dN}{dT} = -\lambda = \frac{d\epsilon_r}{dT} \frac{1}{(\epsilon_r - 1)[(\epsilon_r - 1)\gamma + 1]} \quad (2.51)$$

The temperature coefficient of  $\epsilon_r$  is thus related to the coefficient of expansion in accordance with (2.51) if  $\gamma$  and  $\alpha$  are assumed to be temperature-independent. Now in the vicinity of the critical temperature  $\theta_f$ , the dielectric constant  $\epsilon_r \gg 1$  and since, according to section 2.6, the internal field constant is of the order of unity (or perhaps larger in ferroelectric materials), one may write (2.51) in the approximate form

$$\frac{d\epsilon_r}{dT} \cong -\lambda\gamma\epsilon_r^2 \quad (2.52)$$

How does the dielectric constant near  $T = \theta_f$ , but in the region  $T \geq \theta_f$ , vary with temperature? Evidently for  $T = \theta_f$  we have  $N(\theta_f)\alpha\gamma/\epsilon_0 = 1$  so that according to (2.48)  $\epsilon_r(\theta_f) = \infty$ . Hence we obtain from (2.52)

$$\int_{\epsilon_r = \infty}^{\epsilon_r} \frac{d\epsilon_r}{\epsilon_r^2} = -\lambda\gamma \int_{\theta_f}^T dT$$

so that upon integration we obtain

$$\epsilon_r = \frac{1/\lambda\gamma}{T - \theta_f} \quad \text{for } T > \theta_f \quad (2.53)$$

We see that this expression is exactly of the form (2.43); i.e., this model provides us with the experimentally observed Curie-Weiss law for the dielectric constant above the critical temperature (see also Fig. 2.19). Note, however, that in this model the ferroelectric Curie temperature  $\theta_f$  is identical with the temperature  $\theta$  in the Curie-Weiss law, whereas experimentally  $\theta$  is usually a few degrees lower than  $\theta_f$ .

It is of interest to note that for BaTiO<sub>3</sub> the coefficient of expansion  $\lambda \cong 3 \times 10^{-5}$  per degree and the observed Curie constant  $1/\lambda\gamma \cong 10^5$ . Consequently, there is also reasonable agreement as far as the order of magnitude of the Curie constant for BaTiO<sub>3</sub> is concerned between the model and experiment, if one assumes  $\gamma \approx 1$ .

## 2.10 Piezoelectricity

In our previous discussions we have seen that an applied electric field induces dipole moments in atoms or ions, and generally displaces ions relative to each other. Consequently, the dimensions of a specimen undergo slight changes. Mechanical stresses also change the dimensions



of a specimen but in general such changes do not produce a dipole moment. In other words, in most materials dielectric polarization produces a mechanical distortion, but a mechanical distortion does not produce polarization. This electromechanical effect, which is present in all materials, is called *electrostriction*. In purely electrostrictive materials, the mechanical deformation produced by a polarization in a given direction is the same as that produced by a polarization in the opposite direction; i.e., mechanical changes can be expressed as a series expansion containing only terms with *even* powers of  $P$ . A simple example of a material with only electrostrictive properties is given in Fig. 2.28. Note that the basic unit from

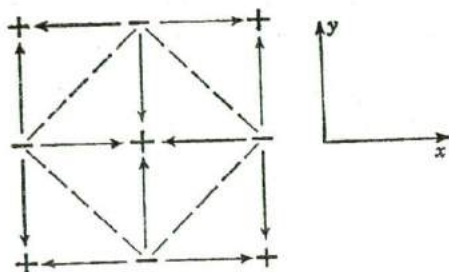


Fig. 2.28. A two-dimensional square lattice with only electrostrictive properties. Application of a field along the positive  $x$ -direction produces the same mechanical deformation as a field along the negative  $x$ -direction. The dashed square represents the basic unit, and has a center of symmetry.

which this material can be built contains a *center of symmetry*; i.e., starting from the center and drawing a vector to one of the surrounding ions, one finds a similar ion at a position corresponding to a vector of equal length drawn in the opposite direction.

There are solid dielectric materials, however, for which the sign of a mechanical deformation produced by a polarization  $P$  changes when the direction of the polarization is reversed. Such mechanical deformations then contain at least one term with an *odd* power of  $P$ . These materials do become polarized upon application of a mechanical stress and are called *piezoelectric*; they are of practical importance because they permit *conversion of mechanical into electrical energy* and vice versa. A two-dimensional example of such a material is represented in Fig. 2.29. The basic unit from which this material can be built evidently *lacks a center of symmetry*, and this is a requirement for a piezoelectric material.

We note that if in Fig. 2.29 we apply a tension along the  $x$ -direction, the angle  $\theta$  will increase, thus giving rise to a polarization in the positive

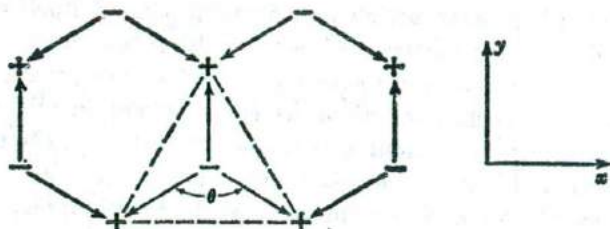


Fig. 2.29. A two-dimensional structure with piezoelectric properties; the dashed triangle lacks a center of symmetry.

$y$ -direction. But if the unit is compressed along the  $x$ -direction,  $\theta$  will decrease and the polarization will lie along the negative  $y$ -direction. On the other hand, application of tension or compression to the basic unit in Fig. 2.28 produces no polarization at all, because of the symmetry of the unit. For a detailed discussion of the piezoelectric effect the reader is referred to the books listed below.

### References

- C. J. F. Böttcher, *Theory of Electric Polarization*, Elsevier, Amsterdam, 1952.
- P. Debye, *Polar Molecules*, Dover, New York, 1945.
- A. von Hippel, *Dielectric Materials and Applications*, Technology Press, Cambridge, Massachusetts, and Wiley, New York, 1954.
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### Problems

2.1 A charge of  $Q$  coulombs is distributed homogeneously over the surface of a sphere with a radius of  $R$  meters; the sphere is in vacuum. Find the flux density  $D$ , the field strength  $E$  and the potential  $V$  as a function of the distance  $r$  from the center of the sphere for  $0 \leq r \leq \infty$ ; assume  $V(\infty) = 0$ .

2.2 A charge of  $Q$  coulombs is distributed homogeneously throughout the volume of a sphere of radius  $R$  meters; the sphere is in vacuum. Find the flux density  $D$ , the field strength  $E$  and the potential  $V$  as a function of the distance from the center of the sphere for  $0 \leq R \leq \infty$ ; assume  $V(\infty) = 0$ .



**2.3** Find the capacitance  $C$  of an isolated conducting sphere of radius  $R$  meters in vacuum. If the sphere is charged with  $Q$  coulombs, what is the energy stored? Assume the potential is zero at infinity.

**2.4** Consider two coaxial metal cylinders of radii  $R_1$  and  $R_2$ . The space between them is filled with a dielectric with a relative dielectric constant  $\epsilon_r$ . The potential difference applied between the two cylinders is  $V$  volts. Find the charge on the cylinders and the capacitance of the system per meter length (neglecting end effects).

**2.5** Electrolytic condensers are manufactured by anodic oxidation of aluminum; the thickness of the aluminum oxide layer formed in this manner is proportional to the anode voltage employed, and amounts to approximately 0.1 micron per 100-volt anode voltage. Find the approximate capacitance for a strip of aluminum of 5 cm by 40 cm, oxidized on both sides to an anode voltage of 500 volts if  $\epsilon_r = 8$  for  $\text{Al}_2\text{O}_3$ .

**2.6** In the design of oscillator-tank circuits one is frequently faced with the requirement of temperature-independent tuning. If  $L$  and  $C$  are the equivalent self inductance and capacitance of the circuit, show that this requirement may be expressed mathematically as

$$\frac{1}{L} \frac{dL}{dT} + \frac{1}{C} \frac{dC}{dT} = 0$$

where  $T$  is the temperature.

**2.7** A condenser of 1 microfarad contains titanium oxide ( $\text{TiO}_2$ ) as a dielectric with  $\epsilon_r = 100$ . For an applied d-c voltage of 1000 volts, find the energy stored in the condenser as well as the energy stored in polarizing the titanium oxide. Answer the same questions for a 1-microfarad mica condenser, assuming a dielectric constant  $\epsilon_r = 5.4$  for mica.

**2.8** Consider a neutral system of point charges,  $Q_1, Q_2, \dots, Q_i, \dots$ , which are located at the endpoints of a set of vectors  $\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_i, \dots$  drawn from the origin of a coordinate system. Show that the dipole moment  $\boldsymbol{\mu} = \sum_i Q_i \mathbf{r}_i$  is independent of the choice of the origin of the coordinate system. (Hint: shift the origin to another point, write down an expression for  $\boldsymbol{\mu}$  in the new system, and show that  $\boldsymbol{\mu}_{\text{new}} = \boldsymbol{\mu}_{\text{old}}$ ).

**2.9** With reference to a two-dimensional Cartesian coordinate system  $x, y$ , four point charges are located as follows: a charge of  $Q$  coulombs in the point  $(0, 0)$ ;  $-Q$  in  $(1, 0)$ ;  $2Q$  in  $(1, 1)$ ; and  $-2Q$  in  $(0, 1)$ ; the numbers refer to meters. Find the magnitude and direction of the dipole moment of the system.

**2.10** An electrolytic condenser consisting of an oxidized aluminum sheet with an effective surface area of  $400 \text{ cm}^2$  has a capacitance of 8 microfarads; the dielectric constant of  $\text{Al}_2\text{O}_3$  is  $\epsilon_r = 8$ . A potential difference of

10 volts is applied between the aluminum and the electrolyte. What is the field strength and what is the total dipole moment induced in the oxide layer?

**2.11** A particle of charge  $Q$  coulombs is bound elastically to an equilibrium position with a force constant  $f$  newton  $m^{-1}$ . What is the polarizability of the system?

**2.12** Assuming that the polarizability of an argon atom is equal to  $1.43 \times 10^{-40}$  farad  $m^2$ , calculate the relative dielectric constant of argon at  $0^\circ C$  and 1 atmosphere.

**2.13** According to wave mechanics, an electron in the ground state of a hydrogen atom corresponds to a charge distribution given by expression (1.11). Assuming that the form of the charge distribution remains constant for small applied electric fields, calculate the polarizability of the hydrogen atom by the method used in section 2.3; assume that the displacement of the charge cloud relative to the nucleus  $\ll r_1$ . Compare the answer with expression (2.12).

**2.14** An atom of polarizability  $\alpha$  is placed in a homogeneous field  $E$ . Show that the energy stored in the polarized atom is equal to  $\frac{1}{2}\alpha E^2$ .

**2.15** An atom has a polarizability of  $10^{-40}$  farad  $m^2$ ; it finds itself at a distance of 10 angstroms from a proton. Calculate the dipole moment induced in the atom and the force with which the proton and the atom attract each other.

**2.16** A sealed-off vessel with two electrodes to measure the dielectric constant of a gas has a pressure of 760 mm of mercury at  $300^\circ K$ . The dielectric constant at  $300^\circ K$  is found to be  $\epsilon_r = 1.006715$ ; at  $450^\circ K$ ,  $\epsilon_r = 1.005970$ . Find the number of molecules in the gas per  $m^3$ , the dipole moment of the molecules and the polarizability of the molecules.

**2.17** A point dipole of  $\mu$  coulomb m finds itself at a distance of  $a$  meters from the center of an atom of polarizability  $\alpha$  farad  $m^2$ ; the direction of  $\mu$  is parallel to the line joining the dipole and the center of the atom. Find the dipole moment induced in the atom.

**2.18** Repeat problem 2.17 for the configuration in which  $\mu$  is perpendicular to the line joining the dipole and the center of the atom.

**2.19** The centers of two identical atoms of polarizability  $\alpha$  farad  $m^2$  are separated by a distance of  $a$  meters. A homogeneous electric field  $E$  is applied in a direction parallel to the line joining the centers of the two atoms. Find the internal field  $E_i$  at the position of each of the atoms. If  $\alpha = 2 \times 10^{-40}$  farad  $m^2$  and  $a = 5 \times 10^{-10}$  m, what is the ratio between  $E_i$  and  $E$ ?



**2.20** Repeat problem 2.19 for an applied field  $\mathbf{E}$  perpendicular to the line joining the centers of the two atoms.

**2.21** Consider a solid containing  $N$  identical atoms per  $\text{m}^3$ ; the polarizability of the atoms is  $\alpha$  farad  $\text{m}^2$ . Assuming a Lorentz internal field, derive the Clausius-Mosotti relation.

**2.22** A solid contains  $5 \times 10^{28}$  identical atoms per  $\text{m}^3$ , each with a polarizability of  $2 \times 10^{-40}$  farad  $\text{m}^2$ . Assuming that the internal field is given by the Lorentz formula, calculate the ratio of the internal field to the applied field.

**2.23** Consider the following two infinite arrays of identical equidistance *point* dipoles:

$$\begin{array}{ccccccc} \dots & \rightarrow & \rightarrow & \rightarrow & \dots & \rightarrow & \dots & \text{(ferroelectric)} \\ \dots & \uparrow & \downarrow & \uparrow & \dots & \downarrow & \dots & \text{(antiferroelectric)} \end{array}$$

The distance between neighboring dipoles is the same in the two configurations. From an examination of the field produced at the position of a given dipole by all other dipoles in the array, argue which of the two configurations is the more stable one.