

1. ORDER AND DISORDER

The study of crystalline materials has played a prominent role in the traditional approach to solid state physics. The crystallinity introduces considerable simplifications into the description of structure and the formulation of theories for the physical properties. Therefore it is natural that the study of solid state physics emerged from crystallography and that the basic theories were formulated for the case of crystalline matter.

However, many practical applications use materials that are weakly or strongly disordered. For example the doping of semiconductors, which is necessary in microelectronics technology, can be viewed as a departure from perfect crystallinity. Hence a deeper understanding of the properties of disordered materials is desired in various technological applications. At the same time effects of disorder are studied intensively from the viewpoint of fundamental physics. Many of the challenging problems within solid state physics today are in some way or other connected to disorder.

Weak disorder may be defined as a perturbation of the perfect crystalline order. To this category belong defects, vacancies and dislocations which are frequently observed in real materials. In polycrystalline materials the grain boundaries display a more disordered configuration of atoms than the grains.

Strong disorder signifies a marked departure from crystalline order. The basic property of amorphous materials is that they do not possess any long range translational order. There exists an element of randomness in the atomic positions. The length scales over which order or disorder persists are also of interest. As we will see many materials possess a local order over length scales of a few atoms or molecules, but are disordered on larger length scales. Inhomogeneous materials, such as multiphase materials, composites and porous materials can be regarded as disordered and homogeneous on sufficiently large length scales, and the inhomogeneities lead to more local strong disorder on mesoscopic (nm- μm) length scales.

Materials that possess disorder over a range of length scales have been studied intensively in recent years. They can often be modeled as random fractals. Fractals are mathematical constructs that exhibit dilation symmetry. This means that they are self-similar, i.e. they look the same on different length scales. For random fractals, which are more disordered, this statement is true in a statistical sense only. Modeling of a complex structure by a fractal leads to considerable simplifications, since it can be

described by a small set of parameters, i.e. a fractal dimension and lower and upper cutoff lengths in the simplest case. Below the lower and above the upper cutoff the material can be regarded as homogeneous.

1.1 Ordering rules

Now we put the discussion of order and disorder on a more formal basis and consider so called ordering rules. Start with a collection of objects labelled with an index h having properties p_h . An ordering rule then relates the property p_h of one object to the same property of another object. Perfect order is then defined as follows:

In the case of perfect order the properties p_h of all objects can be derived from knowledge of only one p_h , by repeated application of the ordering rule.

Example 1: Let the property be the positions of atoms in a perfect crystal. The translational symmetry of the crystal structure is the ordering rule. From the position of one atom and the knowledge of the crystal structure all atomic positions can be derived.

It is clear that this is not the case for all structures. If there exists some randomness in the atomic positions, then it is impossible to predict the positions from an ordering rule. However, a more or less detailed statistical description of the structure might be obtained. Hence we can speak of different degrees of disorder depending on how detailed a description of the structure it is possible to obtain. Degrees of disorder, or partial ordering, may be quantified by a so called order parameter.

Example 2: Consider a crystalline binary alloy AB. It may exhibit different degrees of disorder. The two species, A and B, may alternate regularly on the crystal lattice, leading to an ordered structure. Alternatively, the two kinds of atoms may be distributed over the lattice points according to a probabilistic rule or even completely at random. Let C_A be the fraction of A atoms and r the fraction of those that are in the positions they would occupy if a state of perfect order prevailed. We can now define the order parameter for this problem by the relation

$$\xi = (r - C_A) / (1 - C_A) \quad (1.1)$$

This quantity is obviously unity in the case of complete order and zero in the case of a completely random distribution over the lattice points. Hence ξ is a measure of the degree of disorder.

Above we have considered structural and chemical disorder but the concept of disorder can also be applied to various properties of a material that are varying in an irregular way in space. Fig. 1.1 depicts four different kinds of disorder. The structural or topological disorder is characterized by the absence of long range order and translational periodicity. In the case of magnetic disorder, the spin exhibits different values at each point on a lattice. A similar situation occurs in dipolar solids and liquids where the dipole moments exhibit orientational disorder. Chemical or compositional disorder characterizes a large class of materials such as alloys, mixtures, composites and porous materials. We will have much to say about such materials later. Finally, vibrational disorder refers to the departure of the instantaneous atomic positions from lattice points due to the thermal vibration of the atoms. This latter case we will not consider the further, since the average positions coincide with the lattice points. Furthermore the values of physical quantities may be statistically distributed over a structure and hence exhibit disorder.

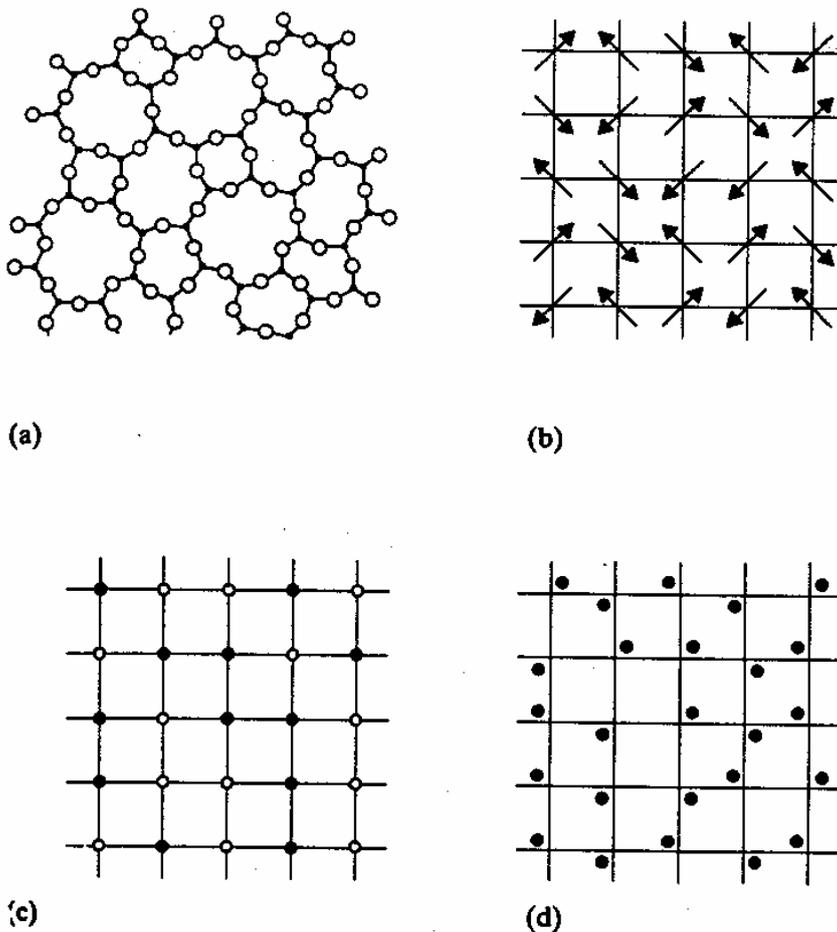


Figure 1.1 Illustration of various types of disorder; (a) structural, (b) orientational, (c) compositional and (d) vibrational (from Elliott, p. 3).

In this course we consider mainly structural and compositional disorder in non-crystalline solids.

1.2 Classification of disordered materials

In this section we attempt a simple classification of disordered materials and define some important concepts. We define amorphous materials as materials that do not possess any long range translational symmetry. As mentioned above a short range ordering often exists, for example due to the constraints of chemical binding.

Liquids are perhaps the simplest case of disordered materials, because the structural randomness is most pronounced in this case. Even so, a short range order is present manifesting itself in a certain number of nearest neighbors of a given atom. The physics of liquids is an extensive subject and interesting in its own right. Since the present text deals with solids we will not consider the properties of liquids further.

Amorphous solids are solid materials exhibiting an amorphous structure. They can be produced in thin film form by evaporation, sputtering and chemical vapor deposition, under the appropriate conditions. A low substrate temperature promotes an amorphous structure. A material of technological importance is amorphous silicon, which can be doped with H and is of interest for photovoltaic applications. We will have much more to say about amorphous materials later.

A glass is an amorphous solid which exhibits a glass transition. It has a similar structure as the liquid from which it is derived by cooling below the freezing point, without crystallization. Glasses can be produced by rapid cooling from the melt (melt quenching). Important examples encompass vitreous silica, chalcogenide glasses (based on S, Se, Te compounds) and metallic glasses.

Composites are solids having two or more constituents. They are of large technological interest since many physical properties can be tailored as needed by mixing materials with different properties. Nanocomposites produced by compacting nanometer sized particles produced by gas evaporation is today a very hot scientific subject. Unique mechanical properties can be displayed and studies of other physical properties are expected to give rise to novel applications. A related class of materials are porous solids, where one of the constituents is air. Composites where one of the phases consists

of complex aggregates as well as many porous solids have been modeled by fractal geometry over a range of length scales.

1.3 Entropy and disorder.

Above we have considered the amount of disorder in a certain configuration of our system. However, physical systems are considered to be in a certain thermodynamic state, specified by the values of the thermodynamic variables. There are a vast number of configurations that are compatible with a certain thermodynamic state. That means that we have to compute ensemble averages of the order parameter to characterize the degree of disorder. Equivalently, we can use the time average. The system fluctuates from moment to moment and the time average can often be regarded as equivalent to the ensemble average.

Entropy is a thermodynamic quantity that is intimately connected to the degree of disorder. It is given by

$$S = k_B \ln W \quad (1.2)$$

where W is the number of microscopic states compatible with the macroscopic thermodynamic state of the system. In our case we may see it as a measure of the number of configurations of the system that are permitted by the disorder.

Example 1: As more vacancies are introduced into a crystal by heating, the number of possible arrangements of the vacancies over the lattice points increases. Hence W and the entropy also increase. The contribution to the entropy from the vacancies is called configurational entropy, because its origin lies in spatial structure. The configurational entropy gives a contribution to the free energy that is opposite in sign to the energy of vacancy formation. This leads to an equilibrium characterized by a certain temperature dependent vacancy concentration.

Example 2: When two fluids are mixed, the number of possible configurations increases also in this case. The corresponding contribution to the entropy is called entropy of mixing, and the consequences are similar to those of example 1.

1.4 The glass transition

As mentioned above, many materials can be made into glasses by rapid cooling from the liquid state. They solidify in to an amorphous state because the structural relaxation time needed for the material to enter into the energetically favourable crystalline state is much longer than time scales of experimental relevance. A practical, but rather arbitrary, definition of a solid is that the viscosity should exceed $10^{13.6} \text{ Nsm}^{-2}$. Hence the temperature at which the material has this viscosity is used as a definition of the glass transition temperature, T_g . This definition corresponds approximately to a relaxation time of one day. The glass transition is a subject of intensive scientific interest. Although various models for it have been proposed, it is still not understood in detail.

The glass transition is not considered to be a thermodynamic phase transition. It is rather a more or less steep change in thermodynamic quantities (such as the heat capacity and the thermal expansion coefficient) from solid-like to liquid-like values in a region around the glass transition temperature, T_g . As the liquid is cooled below its melting point, it becomes supercooled. The transition to the glassy state occurs at a considerably lower temperature. The volume as a function of temperature exhibits a change of slope at T_g , but not a discontinuity as in the case of crystallization. The glass transition temperature is several hundred degrees above ambient in the case of oxide glasses, but for organic materials like polymers it can be close to room temperature or even lower.

The viscosity varies rapidly with temperature in the region of the supercooled liquid. Empirically it has been found to vary as

$$\eta(T) = \eta_0 \exp(-A/(T - T_0)),$$

where A and T_0 are constants. The glass transition temperature is always higher than T_0 . The equation is known as the Vogel-Tammann-Fulcher (VTF) law. Similar equations hold for the structural relaxation time and the ionic conductivity. The usual thermally activated (Arrhenius) behaviour is obtained as $T_0 \rightarrow 0$. Some glasses follow a close to Arrhenius dependence of the viscosity but the VTF law is more common.

The challenging problem of the glass transition has stimulated many theoretical ideas. The free volume theory regards the supercooled liquid to consist of solid-like and liquid-like cells. The latter ones contain a so-called free volume which can be redistributed amongst them. The number of liquid-like cells decreases as T decreases,

until at the glass transition, the properties of the material are dominated by the solid-like cells. The mode-coupling theory presents a general scenario for relaxations in supercooled liquids. In particular it presents a dynamical transition at a certain critical temperature. The situation as regards comparison with experiment appears to be somewhat unclear, with both agreement and disagreement in different cases.

More details can be found for example in the book by Elliott (see reference list).

1.5 The origin of disorder.

The occurrence of disordered structures can be seen as the outcome of an interplay between physical laws and randomness. A completely random structure would in a sense be perfectly disordered, but in practise this is not attained due to the presence of physical constraints. Even in liquids there are significant interactions between the molecules leading to a local ordering at short length scales. In composites containing particles of phase A dispersed in a matrix, B, a departure from randomness is introduced already by the fact that the particles may not penetrate each other.

Glassy and amorphous materials exhibit a short range order due to chemical constraints. The number of covalent bonds per atom is the same in crystalline and disordered structures. Actually, non-satisfied bonds, so called dangling bonds, often occur as defects in amorphous materials, but we neglect them for the moment.

A variety of seemingly random aggregation processes lead to beautiful fractal aggregates exhibiting a very complex structure. For example particles may perform a random walk until they stick to a growing aggregate. Also here both randomness and physical law is at work. The sticking of the particles to one another is due to attractive forces, such as those originating in van der Waals or dipolar interactions.

General references:

Barabasi, A.-L. And Stanley, H.E., Fractal Concepts in Surface Growth,, Cambridge Univ. Press 1995.

Bunde, A. and Havlin, S. (eds) Fractals and Disordered Systems, Springer, Berlin, 1991.

Cusack, N.E., *The Physics of Structurally Disordered Matter*, Adam Hilger, Bristol, 1987.

Elliott, S.R., *Physics of Amorphous Materials*, Longman, London, 1984.

Mott, N.F. and Davis, E.A., *Electronic Processes in Non-Crystalline Materials*, Clarendon, Oxford, 1979.

Zallen, R., *The Physics of Amorphous Solids*, Wiley, New York, 1983.

Ziman, J.M., *Models of Disorder*, Cambridge Univ. Press, Cambridge, 1979.

These references are referred to by author name only in the text. They are available in the reference shelf for the course in the Division of Solid state physics library.