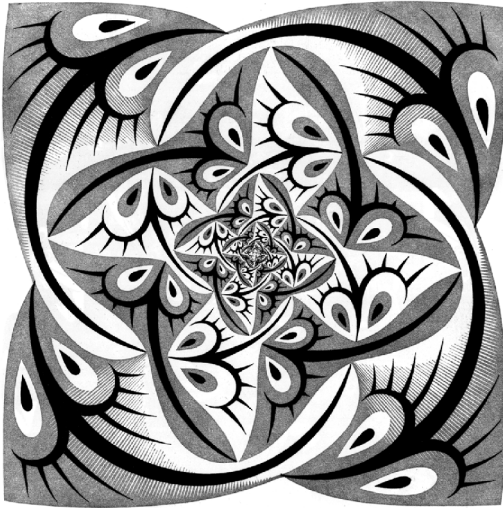


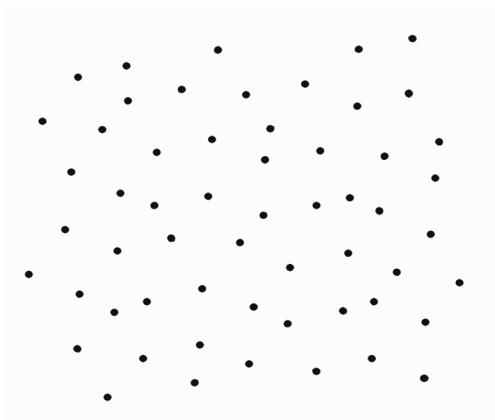
## 2. Structural Order

### 2.1 Order and Disorder

Order and disorder are rather complex concepts with various and sometimes contrary exceptions and shades and this makes it somewhat difficult to give them a generally valid definition. The dictionary defines order as “the arrangement of objects in position, or of events in time” or, more generally, “the manner in which one thing succeeds another” [2.1].



**Fig. 2.1.** An example of ordered, but not regular, structure is given by “Path of Life II” by M.C. Escher (1958). “From the centre, representing the limit of infinitely small, four rows of fish (rays) protrude, in spiral form, swimming head to tail. The four largest examples, enclosing the square surface, change direction and colour: the white tails are still part of the school that comes from the centre while the grey heads are pointed towards the inside and are part of the grey rows pointed towards the centre.” (M.C. Escher’s “Path of Life II” © 2002 Cordon Art B.V.-Baarn-Holland. All rights reserved)



**Fig. 2.2.** Example of aperiodic, non-regular lattice points

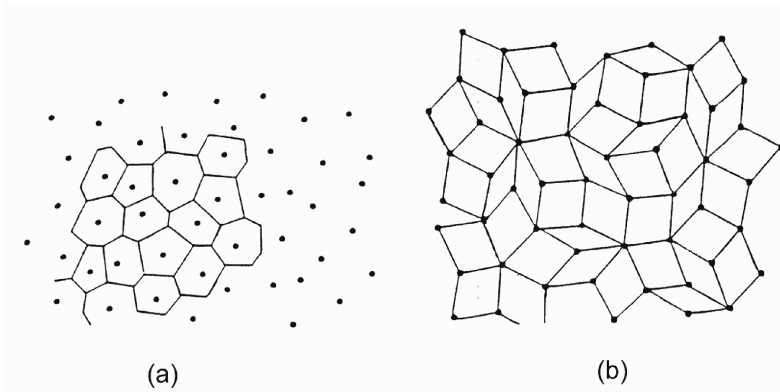
Rather than the general definition of order we are more interested in a series of criteria that can be used in Physics and in particular in analysing the structure of condensed matter, and that can possibly include “objects” in Nature and in art that give the observer the feeling of order.

First of all it is common to consider *order* and *regularity* as equivalent, namely that they belong to the same category and refer to objects in that category. In actual fact the idea that something is regular is geometric and is based on the idea that one or more geometric elements are repeated, whereas order is probabilistic and hinges on the idea of singleness in that a given macroscopic structure corresponds to a single microscopic configuration.

Structures may be ordered but not necessarily regular. An example is Escher’s covering of a flat surface in his xylography called “Path of Life II” shown in Fig. 2.1; another example is given by the proteins which have a single configuration (ordered) with an irregular structure.

The point lattice in Fig. 2.2 is aperiodic and not regular. Figure 2.3 gives two possible ways of covering a flat surface, using different schemes, yet keeping the disposition of the points in Fig. 2.2. In one case the polygons are all different whereas in the other two convex regular polygons give rise to an ordered system in that the arrangement achieved by joining the polygons under certain well defined rules is unique and can be extended indefinitely by further polygon addition.

Crystals are ordered and regular since they can be obtained by periodical translation of an elementary (geometric) cell in space. Excluding the trivial case of a vacuum, crystals constitute the highest degree of three-dimensional order that can be achieved. In a crystal an assembly of innumerable particles (atoms or molecules) is packed in a regular structure along lines in space and on planes in a geometric lattice in order to obtain the highest density possible. With exception to vibrational motion the atoms have a fixed position and are temporarily invariable. As such, from a rheological point of view a crystal is a solid. As we saw in Chap. 1 crystal structures do not change when



**Fig. 2.3.** Two possible plane coverings obtained by conforming with the disposition of the points in Fig. 2.2; (a) using irregular polygons; (b) using two regular polygons (losanges), interconnected by defined rules: the result is a Penrose tiling (aperiodic)

they undergo lattice translations, rotations about axes of different order or reflections in various planes and combinations of reflections and rotations.

The concept of disorder is intuitive and, to some extent, primitive. As such, since it is closely connected to the concept of “casual” it may be defined independently only in a specific context. It is easier to define disorder as a state of absence of, or departure from, the condition of order. The immediate consequence of this approach is that we have to give a better definition of perfect order. From this we have to be able to recognise how much more or less departure from the condition of order is achievable.

## 2.2 Rules of Order

The order of a set of objects is defined with respect to one particular property of the objects. An object may possess  $p$  properties, and the set may be ordered *contemporaneously* with respect to  $i$  properties where  $i$  is less than  $p$ .

In the case of a set of atoms, distributed in space, whose positions are defined by a particular point, namely the centre of mass, and if there is a rule that, when applied to all the atoms, establishes their reciprocal position, provided each atom actually occupies the position it was assigned, then the set is said to be perfectly ordered.

This rule is called the *rule of order*  $\mathfrak{R}$ .

The positional (and orientational) order in decorative motifs is associated with a particular rule of order. In the simplest of cases if these motifs are distributed along a straight line they represent a sort of “crystal” in one dimension.

The *repeated* application of the rule of order  $\mathfrak{R}$  is essential. In fact, in a finite collection it is possible to construct a single arrangement in space

according to a complex rule that defines exactly where each member of the collection is to be placed. The result, however, may be extremely irregular.

To obtain perfect order we must be able to move from one member of the set to another by repeating the same rule. This rule can thus be repeated infinitely and will give us the correct position of the objects that are progressively added to the set.

More generally, a set of objects  $\{O_k\}$ , each having  $n$  properties  $\{p_n\}$ , has perfect order in relation to property  $p_j$  provided there is a rule of order  $\mathfrak{R}$  and that there is at least one object  $O_r$  of which we know  $p_j(O_r)$ . The property  $p_j$  of each of the other objects in the set  $\{O_k\}$ , taken singularly, can be obtained in a unique way with respect to  $p_j(O_r)$  provided that the rule  $\mathfrak{R}$  is applied repeatedly.

This means that the  $\mathfrak{R}$  rule does not contain any factors of probability; it will give the very same result whenever it is applied to  $\{O_k\}$  which, in turn, may be finite or infinite and may also consist of both physical objects (atoms, molecules) and abstract elements, whether they be geometrical (polygons, polyhedra, points, ) or not. Lastly, all the properties  $\{p_n\}$  may include space-time coordinates such as, in Physics, orientational coordinates, the atomic number  $Z$ , which is usually a function of the position  $Z(x)$ , electrical or magnetic dipole moments (atomic or molecular).

In studying condensed matter we must discuss systems that are extended in space and that include many atoms or sets of atoms. In the simple case of an elemental system we are interested in the position of like atoms.

The most important aspect of the rule of order  $\mathfrak{R}$  is that when it is applied to the set in question sequentially we will obtain a *unique* space arrangement. It is clear that in order to achieve order the atoms only have to be the same distance from each other, though this is not a necessity. The application of the rule of order  $\mathfrak{R}$  allows us to substantiate whether the position occupied by any object in the set is correct or not.

The rule of order  $\mathfrak{R}$  must be exact and quantitative. In the simple case of a one dimensional “crystal” we can require that the atoms, seen as random points along a straight line, are distanced from each other by a fixed length, e.g.  $L = 1$  nm. There is no sense in their being just any distance between them provided that the distance is between 1 nm and 1.5 nm; such an imprecise criterion would lead to infinite space dispositions.

In order for space order to be perfect the rule that leads to this space order must be a rule of order namely it generates a unique space disposition when applied repeatedly.

If the objects to be ordered are not identical, e.g. if we are dealing with two different kinds of atoms,  $X$  and  $Y$ , then they can be set out in an ordered manner based on a positional (or topological) rule of order. They may then either be ordered or not with respect to any other property they have in common; among these common properties the chemical order may require that the two species of atoms occupy alternative lattice sites. This sort of order may not occur even though there may be topological order.

*Multiple* order occurs when a set of objects is ordered at the same time with respect to two or more properties. For example, when there is no external magnetic field, atoms of the  $X$  and  $Y$  species, with non-zero magnetic moments, arranged alternatively on simple cubic lattice sites, and having parallel or anti-parallel alignment because of the atomic spin, constitute a set with multiple order, i.e. topological, chemical and magnetic order.

## 2.3 Order Parameters

In most cases physical systems do not exhibit perfect order, nor do they represent complete disorder. On the contrary, the non conformity with a rule of order varies greatly both as regards the degree of order and as regards such properties other than those that lead to the definition of order.

Let's now come back to structural order. Even though a crystal structure may have various kinds of defects 99% of the atoms will lie on lattice sites. The same material in the liquid state will present local order between first and sometimes second neighbours. In sufficiently diluted gases no traces of order are found. If a hypothetical observer ideally inserted an atom in the crystal system then this would more than likely be recognisable since it would occupy an interstitial site. In the case of a gas we would not be able to tell which is the additional atom, not even after a short time interval, owing to the high non-correlated atomic mobility.

On the other hand, it is more difficult to treat a liquid. Owing to the high atomic mobility we presume that the additional atom cannot be identified. However, we can see, at least after a time interval shorter than the diffusion time constant, some atomic correlation in the microscopic arrangement under observation. This is an index of specific local order due to the increased local number density. In this case of limited space order, which, however, leaves no trace over a long distance, we consider, if we start from any arbitrary point, the *radial* extension of local order by implicitly considering that the material is isotropic.

Whenever we refer to systems showing partial order (the most common situation) we must identify how they are disordered and the degree of disorder.

For each kind of phase transition where symmetry is broken we can identify an appropriate macroscopic parameter, called the order parameter  $\eta$ , which gives us a numeric measurement of the degree of order in the system. While we can immediately identify the order parameter in certain transitions it is very difficult to do so in others. For example, in normal liquid-crystalline solid transition the translation symmetry of the liquid phase at high temperature is broken at the transition. In fact, while the space-time average of the microscopic density of a liquid is isotropic, thus it is invariant under all the elements of the translation group, the crystal has a periodic average density and is invariant only under a sub-group of the translation group.

The order parameter, which may be a scalar, vectorial or tensorial quantity, a complex number or any other quantity, appears in the less symmetrical phase in any transition where symmetry is broken whatever the order of the transition, defined according to Ehrenfest. In this scheme the order of a phase transition is given by the lowest order derivative of Gibbs' free energy,  $G$ , which presents a discontinuous change at the transition. In liquid-crystal transition, which is first order, since the slope of the  $G$  curve is discontinuous at the transition temperature, there is an abrupt discontinuity in the state of the system, as reflected by the trend of any intensive variable (volume, density): consequently, the symmetry properties in the liquid and solid phases are not related to each other.

In the case of a continuous transition, such as in paramagnetic-ferromagnetic materials, the rotational symmetry is broken since the spontaneous magnetisation that acts as an order parameter defines a single direction in space. In this case the state of the system changes with continuity and the symmetry properties of the two phases are closely related; usually, though not always, the low temperature phase is the least symmetrical.

Now we consider the continuous order-disorder transition in a binary  $XY$  alloy where, by convention, in the fully ordered configuration the  $X$  atoms occupy the  $\xi$  lattice sites and the  $Y$  atoms occupy the  $v$  lattice sites. Disorder is achieved when the  $X$  atoms move from the  $\xi$  sites to the  $v$  sites and, at the same time, the  $Y$  atoms move from the  $v$  sites to the  $\xi$  sites. No holes and/or interstices are allowed for. In order to quantitatively obtain the degree of order in the system we will take a crystal with  $N$  atoms where

$$\begin{aligned} N_X^\xi &= \text{number of } X \text{ atoms on the } \xi \text{ sites,} \\ N_Y^v &= \text{number of } Y \text{ atoms on the } v \text{ sites,} \\ N_X^v &= \text{number of } X \text{ atoms on the } v \text{ sites,} \\ N_Y^\xi &= \text{number of } Y \text{ atoms on the } \xi \text{ sites.} \end{aligned}$$

Thus the following stand

$$\begin{cases} N = N_X + N_Y \\ N_X = N_X^\xi + N_X^v \\ N_Y = N_Y^\xi + N_Y^v \\ N_X^v = N_Y^\xi \end{cases} \quad (2.1)$$

where  $N$ ,  $N_X$  and  $N_Y$  are constant during the order-disorder transition (we do not consider there may be some chemical reaction between the  $X$  and  $Y$  atoms).

$$c_X = \frac{N_X}{N} \quad \text{and} \quad c_Y = \frac{N_Y}{N}$$

are the atomic fractions of the  $X$  and  $Y$  atoms respectively of the crystal, and

$$f_I^i = \frac{N_I^i}{N_I}, \quad \text{where } I = X, Y; \quad i = \xi, v$$

are the fractions of the  $I$  type of atoms that occupy (correctly) the  $i$  sites, calculated with respect to the number of  $I$  type of atoms (and not with respect to the overall number of atoms,  $N$ , in the crystal).

The *long range order parameter*  $S$  is obtained using the following relation

$$S = \frac{|f_X^\xi - c_X|}{1 - c_X} \quad (2.2)$$

or, in the same way, by

$$S = \frac{|f_Y^v - c_Y|}{1 - c_Y}. \quad (2.3)$$

$S$  may only take on values in the interval  $[0, 1]$ . In particular, when the crystal has a totally ordered configuration the fraction  $f_X^\xi$  of the  $X$  atoms that occupy the  $\xi$  sites, calculated on the total number of  $X$  atoms, is equal to 1, thus each  $X$  atom occupies a  $\xi$  site; in this case  $S = 1$ .

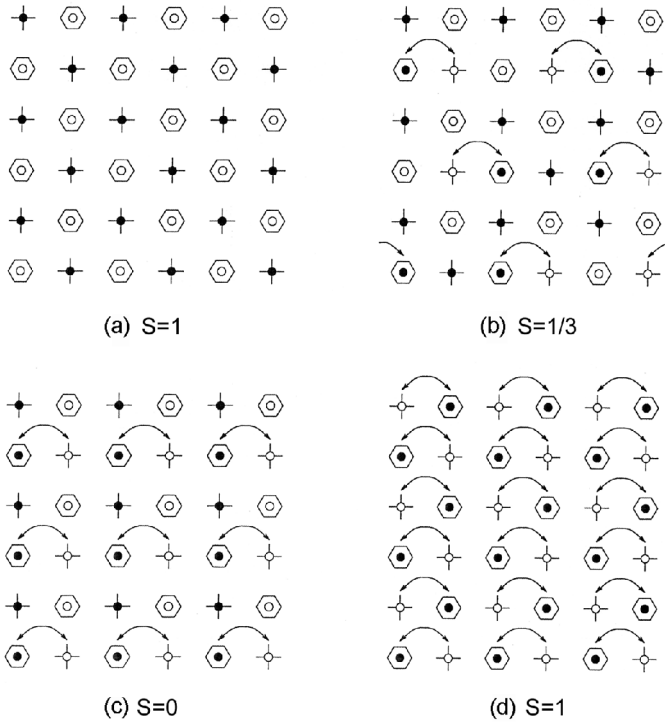
When, though, the crystal has a totally disordered configuration,  $f_X^\xi = c_X$  and  $S = 0$ ; this condition corresponds to the greatest value of  $N_X^v = N_Y^\xi$ : the search for the greatest value is bound by the values in (2.1). The greatest disorder, thus, *does not* correspond to the condition  $f_X^v = 1$  (all the  $X$  atoms on  $v$  sites). For simplicity's sake let us refer to a binary alloy with equiatomic composition. This state would lead to the interchange of all the  $X$  atoms with all the  $Y$  atoms, thus back to complete order.

As an example we shall consider an equiatomic binary alloy  $XY$  lying on a two-dimensional square lattice, as shown in Fig. 2.4. The lattice sites are  $N = 36$ ; for stoichiometric composition  $N_X = N_Y = 18$ , thus  $c_X = c_Y = 0.5$ .

Figure 2.4 shows (part a) the  $\xi$  and  $v$  sites occupied by the  $X$  and  $Y$  atoms in a fully ordered configuration. In this case  $N_X^\xi = 18 = N_Y^v$  and  $N_X^v = N_Y^\xi = 0$ , thus  $f_X^\xi = 1 = f_Y^v$ . The long range order parameter (eqs. 2.2 and 2.3) is  $S = 1$ .

Figure 2.4 shows (part b) partial disorder in the system shown in part (a) of Fig. 2.4. The disorder was obtained by exchanging the positions of  $X$  and  $Y$  atoms that are nearest neighbours, along any line. The scheme shows that alternative lines have a disordered atom arrangement and each position of an  $XY$  atom exchange is separated from the next by an atom in its correct position. Furthermore, the disordered arrangement between contiguous disordered lines is staggered by one atomic position. We impose cyclic boundary conditions; the lattice is thought to be closed on itself. As such we understand why we have to exchange atoms at the edge of the lowest line of the lattice. In this configuration  $N_X^\xi = 12 = N_Y^v$  and  $N_X^v = 6 = N_Y^\xi$ , thus  $f_X^\xi = \frac{2}{3} = f_Y^v$ . The long range order parameter is  $S = 1/3$ .

Figure 2.4 shows (part c) complete crystal disorder. The lines where all the possible exchanges have taken place alternate with perfectly ordered lines.



**Fig. 2.4.** Possible schemes of chemical disordering of an equiatomic  $XY$  binary system on a square lattice ( $\bullet$ :  $X$ ;  $\circ$ :  $Y$ ;  $\vdash$ :  $\xi$ ;  $\square$ :  $v$ ;  $\curvearrowright$ : interchange  $XY$ )

The result is thus  $N_X^\xi = 9 = N_Y^v$  and  $N_X^v = 9 = N_Y^\xi$ ; this corresponds to  $f_X^\xi = 0.5 = f_Y^v$ , thus  $S = 0$ .

Let us take any other disordering scheme, where  $f_X^\xi = 9$ : the long range order parameter has the same value as that of the scheme in part (c) of Fig. 2.4. However, each configuration is characterised by a different value of the short range order parameter  $a(x)$  (see Chap. 4), which gives us an index of the degree of local order around the position of a reference atom.

Figure 2.4 shows (part d) the exchange of all the  $X$  atoms with all the  $Y$  atoms. So,  $N_X^\xi = 0 = N_Y^v$  and  $N_X^v = 18 = N_Y^\xi$  at the same time. In this case  $f_X^\xi = 0 = f_Y^v$ , thus  $S = 1$ . The structure is hence completely ordered; only the observation point has changed.

The quantity  $S$  interpolates between the extremes of complete order and complete disorder and is an example of a scalar order parameter. By using this quantity we can give a quantitative meaning to the expression “partial order” so we can compare different systems with each other.



A *probabilistic* rule of order which does not give us a single result, leads us to partially ordered sets; perfect order, in this case, is obtained only statistically.

In actual fact, even when we consider sets, for example sets of atoms or molecules, for which the property whose degree of order is characterised by a deterministic rule of order, what mostly interests us is the degree of order in the set, considered in a thermodynamic state. Therefore, no particular meaning can be assigned to any specific microscopic configuration among the huge number of those compatible with the set of thermodynamic variables that define the state of the system; we are interested in the ensemble average of the order parameter  $\eta$ .

In principle the calculation for the ensemble average can be simplified provided certain conditions are true. In Statistical Mechanics we usually require that the ergodic condition is true, which can be translated into the equivalence of the ensemble averages with time averages. We can give an example of this equivalence, in general terms, as follows.

We shall start from an initial fixed instant,  $t = 0$ , and consider that the time evolution for two systems,  $\mathbf{P}$  and  $\mathbf{Q}$ , which are identical and isolated and that at the initial time are in two states, 1 and 2, of equal energy.

We will then observe what states  $\mathbf{P}$  and  $\mathbf{Q}$  are in at periodic intervals. For the ergodic condition to be true and having waited long enough, the  $\mathbf{Q}$  system will occupy state 1 and, as of that moment, its statistical evolution will coincide with that of  $\mathbf{P}$ , measured after the initial instant. When we average out very long times, the statistical behaviour of the two systems will become *identical*. The base hypothesis is that the skip frequencies  $V_{mn}$  between any two configurations  $m$  and  $n$  that are compatible with thermodynamic variables are never zero. The isolated system, with fixed constraints, must be able to move from one state to any other of equal energy (accessibility hypothesis).

The equilibrium distribution of the fluctuations of any observable physical quantity, that is its distribution averaged along a sufficiently long period of time so that it becomes independent of time, must be the same for both systems. This means that the characteristics of the equilibrium state of a system depend only on the bonds and on the energy that fix the accessible configurations, whereas any particular microscopic configuration from which system evolution begins is of no importance.

The time averages are necessary because the values of the physical variables that describe the system generally fluctuate from time to time, and thus the degree of order therein fluctuates at the same time. In the statistical set all the variables we want to determine the degree of order of, from the positions to the orientations, to the electrical and magnetic moments, ... present statistical distributions. As such it is clear that if we extract a particular set of values of the variables from the distributions of such a set, the probability that the set we choose provides us with a faithful description of the real degree of order is extremely low.

## 2.4 Cellular Disorder and Topological Disorder

We generally make a distinction between *Long Range Order* (LRO), which extends throughout the structure, and *Short Range Order* (SRO), which involves the shell of the first neighbours of any atom chosen to be the origin, depending on the spatial extension of structural order.

Since the atoms on the surface of a solid, even at thermodynamic equilibrium, undergo different forces compared to those that experience the effect of the presence of atoms in the volume, the interatomic spacing on the surface are different to those in the bulk. The immediate consequence is that there is no lattice order in an agglomerate, with say 100 atoms, where a large number are on the surface. In these cases, however, we will often find short range order.

Atomic clusters are an example of this situation: the kind of structural order in them and their evolution with the dimensions, namely with the number of atoms in the cluster, will be examined in more depth later on. In glassy and liquid systems the experimentally observed short range order is imposed by the chemical nature of the constituents and by the need to achieve geometric atom packings as compact as possible. The structural arrangement among first neighbours gives rise to local order, either Chemical Short Range Order (CSRO), of chemical origin, or Topological Short Range Order (TSRO), of geometrical origin.

*Medium Range Order* (MRO) has progressively gained more importance in amorphous solids, initially in the analysis of elemental semiconductors, silicate and chalcogenide glasses, and later in the structural characterisation of metallic glasses. MRO typically extends on intervals of the order 0.5–2 nm, and this is characteristic of the interaction between second neighbours.

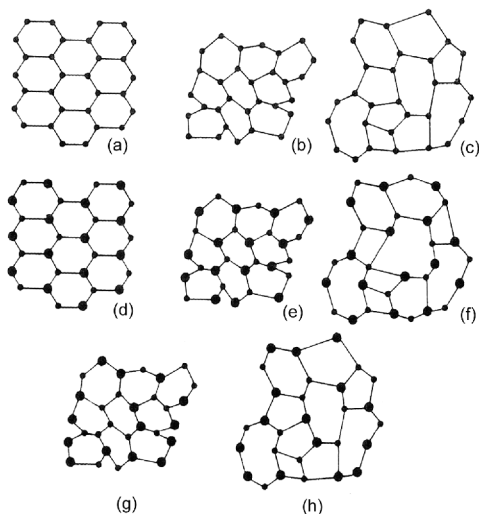
A macroscopic structure with long range crystalline order is subject to periodic translation. Though this is the highest level of structural order possible in condensed matter these crystal structures are usually associated with various kinds of disorder, as seen in Fig. 2.5.

The most widespread sort of disorder is short-range disorder due to localised defects (point and line defects) such as vacancies, di-vacancies, interstitials, substitutional impurity atoms,  $F$  centres, dislocations. Apart from the atoms in the “core” of the defect, the first neighbour atoms of the defect, too, are not to be found on their ideal lattice sites.

Many properties of materials with a technological interest are the outcome of the presence and mutual interaction of these kinds of imperfection. Among these we will find the colour of gems, the electrical properties of semiconductors and the mechanical and thermal properties of metals.

Chemical or compositional disorder, which we have already referred to, can be seen in the  $XY$  binary alloys which undergo order-disorder transitions.

For materials whose atoms have intrinsic magnetic moment, such as ferromagnetic and anti-ferromagnetic materials, disorder is associated with alterations in atomic spin orientation above the critical point of magnetic ordering.



**Fig. 2.5.** Various kinds of disorder that can be found in a perfect crystal (a) elemental and (d) made of an equiatomic binary alloy; (b) the bond lengths vary generating bond disorder; (c) bond coordination also varies giving rise to dangling bonds and topological disorder; (e) (f) (g) and (h) present various combinations of the above kinds of disorder with varying weights

Disorder may occur in molecular arrangement as well. This is observed, for example, in the semiconductor compound CsPb, of which it has recently been noticed that melting takes place in two distinct phases. At higher temperature the system is a normal liquid, showing orientational and translational disorder; at lower temperatures, structural units  $\text{Cs}_4\text{Pb}_4$ , each characterised by a tetrahedron ( $\text{Pb}_4^{4-}$ ) inside a tetrahedron ( $\text{Cs}_4^{4+}$ ) oriented in the opposite direction have been identified. Such relatively large units, possessing rotational symmetry, have long range translational order though they are subject to fast re-arrangement along four non-equivalent directions in the lattice. Such an intermediate phase, called a plastic crystal, is common of organic molecular solids and has also been observed in the NaSn semiconductor.

At a temperature  $T = 0$  K, in those systems with chemical or orientational disorder, both molecular and involving atomic spins, perfect order sets whereas disorder is prevalent at temperatures above the pertinent critical temperature,  $T_c$ . To understand and to describe the disappearance of order at  $T > 0$  K and the growth of disorder as the system approaches  $T_c$  are both problems that lead to the study of the dependence of the order parameter  $\eta$  on temperature.

The four kinds of disorder we have just examined make up what is called *cellular* disorder. This kind of disorder can be described with reference to a particle placed on an ideal lattice site of a solid. The properties involved are

intrinsic, as in the case of spin direction and chemical composition, or pertain to the presence or absence of defects at low or moderate concentration or, as in the case of thermal motion, regard vibrational displacements.

Unlike a crystal with some degree of disorder, a microscopic sample of an amorphous liquid, or a solid with no defined crystal lattice, is characterised by *topological* disorder. This is the outcome of a relevant property in a liquid, such as the absence of translational atomic motion. In these kinds of system we must consider the *distribution* of the relative positions of the molecules.

Furthermore, if the material is a mixture or an alloy of  $X$  and  $Y$  then it will also have chemical disorder. The preferential attraction of an  $X$  atom for atoms ( $Y$ ) of the other kind leads to the formation of structural units characterised by well defined geometrical shapes, sizes and structures (often based on tetrahedral packing) with partial Chemical Short Range Order.

In the very same way, topologically disordered structures may display complete *order* regarding the spin orientation, as can be seen in saturated amorphous ferromagnetic materials.

## 2.5 Structurally Disordered Materials

The most common class of disordered materials are *liquids*. The greatest problem with liquids is understanding their structural properties and macroscopic behaviour based on atomic and molecular interaction. We shall examine various classes of materials based on their specific microscopic interaction:

- 1) “*simple*” liquids characterised by Van der Waals molecular forces (Ar)
- 2) *fused salts* where the electrostatic ionic forces prevail (NaCl)
- 3) liquid *semiconductors* (Se)
- 4) liquid *metals* whose properties are largely determined by a Fermi gas of conduction electrons

The first investigation, both experimental and theoretical, focused on the structural properties and the equation of state of the simple liquids. Over the last twenty years research has been widened to include semiconductors and metals. However, a clear understanding of the structure of materials in the liquid state is still some way off.

While liquids are usually thermodynamically in a state of equilibrium the amorphous solids, which comprise the second family of macroscopically structurally disordered systems, are not. In fact, in principle any material can be vitrified, provided

$$\Delta G_{\text{proc}} \geq \Delta G_{\text{a-c}} \quad (2.4)$$

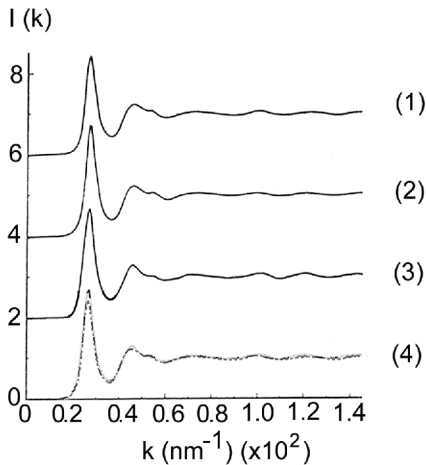
namely that the difference in free energy  $\Delta G_{\text{proc}}$  between the undisturbed crystal and the material condition caused by any external processes (high

pressure compression, deforming and mechanical alloying, irradiation, diffusion at the interface, hydrogen charging up to high concentrations) is greater than the free energy difference between the glassy phase and the crystal phase,  $\Delta G_{a-c}$ . When (2.4) holds the crystal will be disordered. We have to inhibit atoms from returning to the ordered crystalline arrangement associated with the minimum value of free energy in the system. The preparation techniques must thus be able to “arrest” the atomic movement and freeze the atoms in their *metastable* non-equilibrium arrangement. The techniques employed often make use of ultra-rapid cooling; among these techniques we can outline vapour condensation onto a layer kept at cryogenic temperature ( $10^{11} \text{ Ks}^{-1}$ ), ultra-rapid quenching from the liquid ( $10^6 \text{ Ks}^{-1}$ ) quenching a thin surface layer, liquefied by a laser pulse ( $10^8 \text{ Ks}^{-1}$ ) and ion implantation ( $10^{14} \text{ Ks}^{-1}$ ).

When a material can be rendered amorphous by a technique with a given cooling rate it can also be vitrified by any technique characterised by a higher cooling rate. What actually changes is the compositional range through which the amorphisation process occurs; this range increases with the cooling rate. The problem to compare the structure of specimens of the same material, amorphised by different techniques, which could lead to freezing of different degrees of disorder, is still relatively open to discussion. Though not much research has been done on this aspect the amorphous alloys  $\text{Ni}_{63.7}\text{Zr}_{36.3}$ , obtained by melt spinning, and  $\text{Ni}_{65}\text{Zr}_{35}$ , obtained by mechanical alloying, present the very same partial structure factors. Notice that the last is an amorphisation process in the solid state, where the kinetics are very slow compared to the quenching process. For the  $\text{Zr}_{(1-x)}\text{Ni}_x$  alloys, where  $x = 28; 33; 40$  at.%, amorphised by the same two very different techniques, the interatomic distances calculated from the deconvolution of the first peak of the radial distribution function are equal. Samples of the metal glass  $\text{Zr}_{66}\text{Ni}_{34}$ , obtained both by melt spinning and by sputtering, namely condensation from the gas phase, are structurally the same. In the amorphous  $\text{Ti}_{(1-x)}\text{Ni}_x$  systems, where  $x = 24; 35$  at.%, as obtained by solid state amorphization reactions, or by ultra-fast quenching from the liquid state, though the total structure factors differ with composition they are the same as regards differently prepared specimens with the same stoichiometry. Lastly, when the  $\text{CuZr}$  alloy is vitrified using quenching from the liquid state or by low temperature proton bombardment or even by mechanical alloying, no evident structural difference is observed, as shown in Fig. 2.6.

While local structural order in a vitrified metallic system depends on its nature alone, it appears that a number of distinct amorphous phases may form, especially in materials with tetrahedral coordination, such as  $\text{H}_2\text{O}$  and  $\text{SiO}_2$  (see Sect. 3.1).

There are only a few pure elements among the metallic amorphous systems, such as tin, germanium and bismuth. The last two are semi-metals whereas the first has various crystal allotropic forms with free energy values



**Fig. 2.6.** Trend of the scattering intensity  $I(\mathbf{k})$  versus wave vector  $\mathbf{k}$ , in  $\text{Cu}_{50}\text{Zr}_{50}$  samples amorphised by various techniques; (1) energetic particle irradiation; (2) fast quenching from the liquid; (3) mechanical alloying; (4) superposition of curves (1) dots, (2) dashes and (3) continuous line (adapted from [2.3])

close to the amorphous phase, which is thus competitive with them. Even though we often read that amorphous elemental metals have been obtained by way of rapid quenching techniques, we have to treat these results with some degree of caution since if there is even a minimum amount of impurity, mainly gaseous, in the specimens this impurity plays an important role in the heterogeneous nucleation process of amorphisation.

It has been ascertained, though, that chemically pure specimens of some transition metals, such as cobalt, titanium and zirconium, are vitrified when bombarded with low doses, at low current, of accelerated heavy ions with energy in the order of GeV. In these experiments, however, the mechanism that destabilises the crystal structure is *not* lattice disordering, rather it is electronic. The interaction between the projectile and the electrons of the target atoms situated along its trajectory is the relevant process, whereas the atoms themselves will not be displaced from their lattice positions owing to the direct effect of the interaction with the ion.

The physical-chemical structure and properties of many amorphous binary alloys have been studied in depth. Among the considered systems, the simple metal and polyvalent metal alloys ( $\text{CaZn}$ ), the inter-transition metal alloys ( $\text{NiZr}$ ), the noble metal and semiconductor alloys ( $\text{AuSi}$ ) and, lastly, the transition metal and metalloid alloys ( $\text{FeB}$ ). Amorphous alloys with many elements (up to eight) are more easily obtained and have high (meta)stability; such materials have a number of technological applications, but they are not present in basic study owing to their complexity.

Hereafter such terms as *non-crystalline* solids, *amorphous* solids, *vitrified* solids, *glassy* solids and *glass* will be taken as synonyms.

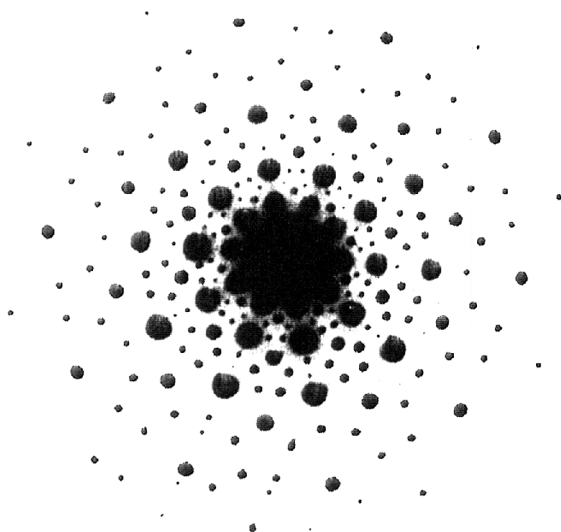
Traditionally, glass is taken to mean an amorphous solid obtained by *supercooling* a liquid until it solidifies. Since the viscosity of a solid is different to that of a liquid, then by way of the macroscopic definition of glass we assume that a value of viscosity of  $10^{12}$  Pas is so high that we can consider any form of fluidity will be inhibited, at least on an infinite time scale as compared to what is experimentally accessible.

From a macroscopic viewpoint, and with reference to the structure, glass is often defined as an amorphous solid. Thus it shows, both in the *length* and in the *angles* that characterise the chemical bonds between first neighbours, a degree of variability. Such a variability, although meeting the constraints of the chemical bond present, which lead to a specific sort of short range order, is, however, sufficient for the constraints are not able to induce long range order.

The silicate glasses such as  $\text{SiO}_2$ ,  $\text{B}_2\text{O}_3$ , and the chalcogenide glasses, including  $\text{As}_2\text{S}_3$ ,  $\text{As}_3\text{Se}$ ,  $\text{GeSe}_2$ , are part of the traditional glass family. On principle, the metallic glasses are a sub-group of the amorphous metallic solids. These solids can be produced using a wide range of methods, which do not necessarily imply the transformation from a liquid to a supercooled liquid state. To this aim, the term metallic glass will hereafter bear the same meaning as the expression non-crystalline metallic solid. This choice is based on the fact that the re-crystallisation of an amorphous metallic material, caused by heating, takes place through very distinct phases of nucleation and growth, exactly like the crystallisation of a liquid and the re-crystallisation of silicate glasses.

Until the mid 1980s liquids and amorphous materials were the only classes of structurally disordered materials known. In actual fact structural disorder was recognised in *atomic clusters*, and a great deal of research has been done on them in the last twenty years. Having produced them, the aim is to characterise the structure, stability and properties, in particular electronic, of free atomic clusters that contain from a few atoms to several tens of thousands of atoms. The changes in properties in these clusters, based on the number of atoms and possibly on their stoichiometry, allow us to experimentally investigate a topic on which, until a few years ago, it was only possible to draw up models and theories. This is the transition from a single atom to an extended solid through the progressively more complex phases of molecule, atomic cluster, surface.

Not too surprisingly we will see that in rare gas atomic clusters the structure of small neutral clusters, during their spontaneous evolution, is non-crystalline; the structure is dominated by tetrahedral and polytetrahedral packing, largely the same as in amorphous materials. Only when the clusters are larger than a certain size will the structures, which are progressively



**Fig. 2.7.** Electron diffraction pattern produced by quasicrystalline  $\text{Al}_{84}\text{Mn}_{16}$

changing with the size of the clusters, take on the fcc structures present in the solidified crystals of the rare gases.

The dependence of the structure on the electronic properties of the constituent atoms, as seen in the small clusters of alkali metals, is also particular. The shell models developed to analyse these clusters are the same successfully used in the study of nuclei and their stability. Basically, the structural stability of the clusters depends on the degree of electronic shell filling, namely on the number of atoms contained in the shell. For those cluster mass numbers which correspond to shell closing, the observed peaks in the mass spectra indicate cluster stability.

In 1984 samples of ribbons of an alloy with  $\text{Al}_{84}\text{Mn}_{16}$  composition were produced using a fast cooling technique. Electron diffraction (Fig. 2.7) showed the presence of rotational three-dimensional fivefold symmetry, that is one of the “forbidden” symmetries in classical crystallography.

From peak width analysis it was clarified that the fivefold symmetry was not an effect due to the presence of multiple twinning, in which case the structure of the materials should have been fcc. It was possible to conclude that in Nature *quasicrystals* with *orientational* long range order and rotational icosahedral fivefold symmetry exist; such a symmetry is responsible for the absence of translational periodicity.

This combination of properties was previously thought to be present only in geometric model structures, both two-dimensional and three-dimensional,



obtained artificially. Among these, in particular, we can mention the Penrose tilings, which uniformly cover the plane provided exact matching rules are used to combine together a small finite number of aperiodic “tiles”, thus generating non regular coverings (Fig. 2.3).

Over the last fifteen years a few hundred compounds have been discovered having quasicrystalline structures, for specific composition and preparation techniques, thus demonstrating that quasicrystal formation is much less pathological than one might think. We are aware of materials with fivefold, eightfold, tenfold and twelvefold rotational symmetry, all of which are “forbidden” by classical crystallography. Much work has been carried out to understand the structural stability of the quasicrystals in relation to the various crystal phases and the glassy state, the microscopic causes at the root of quasiperiodicity and the peculiar physical properties, in particular the electronic ones, of the quasicrystalline materials.

## 2.6 Description of Disorder Through Entropy

Entropy  $S$  is often described as a quantitative index of the disorder present in a system and is frequently used to characterise the glass transition and amorphous materials. From an experimental viewpoint, the trend of the specific heat at constant pressure,  $c_p$ , measured against the absolute temperature when, for instance, liquid-to-solid crystal transition occurs, or when an amorphous solid transforms into a crystal, provides an example of how the reduction in entropy is tied to the reduction in disorder in a given material.

Entropy is connected to the fact that in most thermodynamic states a system is not found to be in a unique, well defined quantum state; it is distributed over a large number of microscopic configurations that are compatible with the considered macrostate, according to a certain probability distribution.

The problem lies in giving the right definition to the quantum multiplicity  $M$ , namely the true number of quantum states over which the probability is distributed at any time.

Entropy  $S$  is defined by

$$S' = k \ln M. \quad (2.5)$$

In the simplest case the probability is distributed uniformly over  $M$  states, thus the probability that a particular state is occupied, is  $p' = 1/M$ , hence we obtain

$$S' = -k \ln p'. \quad (2.6)$$

Using (2.5) and (2.6) entropy supplies us with a measurement of the order of a system, or rather it indicates the lack of detail in the knowledge of the

microscopic state the system is in. Even though the system may be in a *particular* configuration at any time we ignore which state it is in. This is the same as acknowledging that the system is considerably disordered.

If the system is not in a state of equilibrium, or if it can interact with a heat reservoir, then (2.6) must be expressed in general terms with due consideration to the fact that probability  $p'_i$  is not the same value for all the states under examination. The definition of  $S'$  thus becomes, according to Boltzmann–Gibbs

$$S' = -k_B \sum_i p'_i \ln p'_i \quad (2.7)$$

where  $k_B = R/N_{\text{Av}}$ ,  $R$  is the perfect gas constant and  $N_{\text{Av}}$  Avogadro's number. This function is the *average* of (2.6) carried out on the states based on their probability.

In a system at a temperature  $T$  and where  $p_i$  is the equilibrium probability according to Boltzmann,

$$p_i = \frac{\exp[-E_i/k_B T]}{\sum_i \exp[-E_i/k_B T]},$$

the entropy defined in (2.7) becomes the equilibrium entropy

$$S = -k_B \sum_i p_i \ln p_i. \quad (2.8)$$

The states of a macroscopic system usually make up a continuum energy distribution and it is not possible to identify any one countable group of states with the same energy.

The opposite case is more interesting where a macroscopic system has a defined countable number,  $W$ , of isoenergetic configurations.

As such we obtain a configurational contribution to entropy,

$$S_{\text{conf}} = k_B \ln W \quad (2.9)$$

where  $W$  is the number of quantum states of the macroscopic system that are compatible with the set of values for the thermodynamic variables that define the state under examination.  $W$  is thus the number of microstates that are compatible with the macrostate. If we work within the microcanonical ensemble then  $W$  is the number of microstates that are compatible with the volume  $V$ , the number of particles  $N$  and the total energy  $E$  in the system.

For the canonical ensemble,  $W$  is the number of quantum states that contribute significantly to the average energy in the system, where  $V$ ,  $N$  and the absolute temperature  $T$  are fixed.

In a macroscopic system,  $N$  is extremely large, somewhere in the order of  $N_{\text{Av}}$ . As such all the quantum states in the ensemble  $W$ , namely those that are compatible with the macroscopic variables (thus with “reasonable”

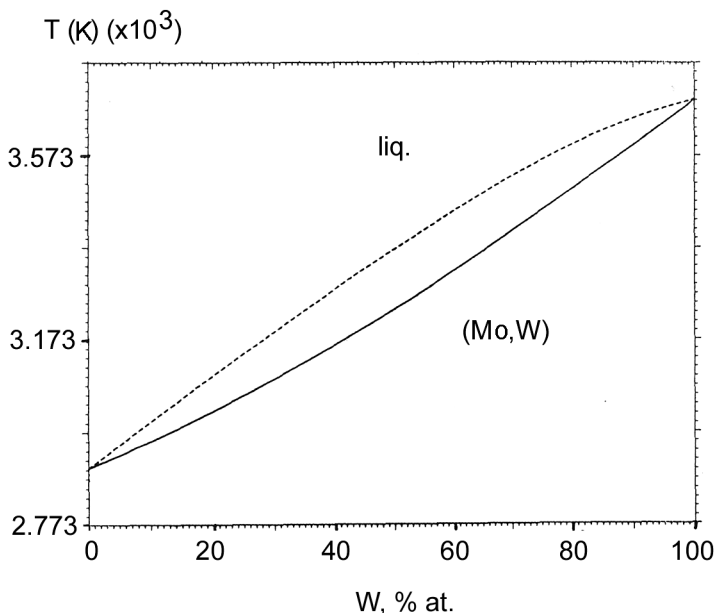
probability they can be realised) define a very narrow band of energy values, centred on the average energy. This means that in practice the energy differences are negligible compared to the average energy.

One example of configurational entropy (i.e. due to the various locations of the component particles in space) of a condensed system, liquid or solid, is given by mixing entropy in an ideal  $XY$  binary system where the mixing entropy  $\Delta H_{\text{mix}}$  is zero and the variation in free energy during mixing is *only* due to entropic change

$$\Delta G_{\text{mix}} = -T \Delta S_{\text{mix}}. \quad (2.10)$$

This representation of an ideal solution, which is easy for us to imagine in a diluted gas with no intermolecular forces, is only acceptable for a solid if the atoms (or molecules) of both species are so similar that we can substitute the atoms of one species with the atoms of the other without causing any appreciable change in either the space structure or in the energy associated with the interatomic interactions in the solution. This implies that the shape and size of the  $X$  and  $Y$  atoms are practically the same and that the interaction energy between pairs of atoms  $X - X$ ,  $Y - Y$ , and  $X - Y$  coincide.

A typical example of such a “mixed crystal” is given by the binary system Mo – W, which shows a continuous series of solid solutions with bcc structure throughout, as can be seen in the phase diagram in Fig. 2.8. The molybdenum



**Fig. 2.8.** Phase diagram of the Mo–W system: an example of a “mixed crystal”

atoms, like the tungsten atoms, can occupy any lattice sites; this gives us a substitutional solid solution, and thus we obtain

$$W = (N_{\text{Mo}} + N_{\text{W}})! / N_{\text{Mo}}! N_{\text{W}}! \quad (2.11)$$

where  $N_{\text{Mo}}$  and  $N_{\text{W}}$  are the number of atoms of Mo and W respectively.

If we refer to a mole of solution, and if  $X_{\text{Mo}}$  and  $X_{\text{W}}$  are the molar fractions of the two elements, then

$$N_{\text{Mo}} = X_{\text{Mo}} N_{\text{Av}}; \quad N_{\text{W}} = X_{\text{W}} N_{\text{Av}}.$$

When we substitute this in eqs. (2.9) and (2.11), and we make use of the Stirling approximation ( $\ln N! \approx N \ln N - N$ ),

$$\Delta S_{\text{mix}} = -R[X_{\text{Mo}} \ln X_{\text{Mo}} + X_{\text{W}} \ln X_{\text{W}}]. \quad (2.12)$$

Since  $X_{\text{Mo}}$  and  $X_{\text{W}}$  are fractions of the unit,  $\Delta S_{\text{mix}}$  is positive, namely an increase in entropy is associated with the mixing of the two subsystems of the atoms Mo and W.

If there is neither interatomic interaction of a chemical nature nor change in volume owing to the mixing process the increase in the system disorder is due solely to the increased uncertainty regarding the position occupied by each atom in the crystal lattice. There are many more possible sites for the atoms to settle on than there are separately available in each of the uniform subsystems Mo and W. From a thermodynamic viewpoint, the above situation is similar to mixing two ideal gases except for the presence of the crystal lattice. Disorder in mixed crystals is much less than topological disorder in an amorphous solid due to the existence of the crystal lattice whose translational periodicity is maintained.

Should the chemical interactions lead to the preferential formation of clusters of atoms, either homogeneous (clustering), or according to some stoichiometric rates (formation of compounds), then we would obtain partial chemical ordering which could lead to a negative change in the system volume. Both these phenomena play an opposite role to the increase in volume associated with mixing and can even lead to negative changes in entropy.

The analysis of mixing ideal *fluids*  $X$  and  $Y$  is very similar to that of solid solutions. In the case of mixing fluids  $X$  and  $Y$ , the uncertainty regarding the position of a given molecule is due to the possibility that the molecule might undergo diffusive translational motions within a certain volume. Once mixing has occurred, there is even greater uncertainty regarding the position of the molecule due to the fact that the volume available for diffusive motion increases. The increase in entropy associated with mixing is calculated by considering the product of each pure macrostate (namely one that has not yet been mixed) of  $X$  for the total number of  $Y$  macrostates necessary to obtain  $W_{\text{mix}}$ .

Since the latter is greater than the sum of  $W_x$  and  $W_y$ , the change in entropy associated with mixing is positive.

Even when we introduce local disorder into a crystal, when we form lattice vacancies while heating the crystal itself, configurational entropy will increase. For a fixed volume  $V$  and number of atoms  $N$ , as the number of vacancies increases so does the number of equally probable alternative positions for the vacancies on the lattice sites, obtained through an atomic jump mechanism. If we assume that the vacancies are equivalent to an atomic species the resulting system is obtained by mixing vacancies and atoms in the crystal. The total change in the system entropy is

$$\Delta S = -R [X_v \ln X_v + (1 - X_v) \ln(1 - X_v)] + X_v \Delta S_v. \quad (2.13)$$

Here  $X_v$  represents the molar vacancy fraction we have introduced and (2.13) coincides with (2.12) for mixing entropy in an ideal system, except for the second term that represents the (small) contribution to thermal entropy from a mole of vacancies  $\Delta S_v$ . This term is associated with the slight change in the vibrational frequency of the atoms surrounding a vacancy in the lattice, which is due to the substitution of a vacancy for an atom.

The aim of this discussion, using the examples, is to clarify that, though strictly connected, disorder and entropy are qualitatively different from each other. Entropy is a variable that is intrinsically statistical. The occupational probability associated with a particular state under consideration is an integral part of its definition. As such there is no reason to discuss the entropy of a single configuration whereas determining the amount of disorder associated with that very same configuration does constitute a significant problem.

If the specific configurations of the system exhibit disorder then the examination of the statistical ensemble of the systems will allow us to calculate a *finite* entropy which, in turn, will give us the number of configurations that are compatible with the degree of disorder.

Since a fluid is normally in a state of thermodynamic equilibrium it is possible to calculate its thermodynamic properties using methods that, though complicated, belong to equilibrium statistical mechanics.

The remaining non-crystalline matter (ordinary glasses and metals, systems with frozen spins, quasicrystals ...) *cannot* be found, normally, in thermodynamic equilibrium since it is obtained through fast quenching techniques. The atomic motion is frozen during the fast cooling of the system so that the atoms do not have enough time to reach configurations of equilibrium at the final temperature. Fast cooling, in fact, does not inhibit thermal motions: the atoms vibrate around their positions just as, in a magnetic system, the spins can be realigned. However, the thermal excitation is not sufficient to cause the redistribution of atom positions. The system is thus metastable, in that the atom positions coincide with *relative* minima of the free energy, unlike the lattice positions, which correspond to absolute minima. Thus, an amorphous system is subject to atomic relaxation motions towards equilibrium configurations, with very low atomic re-arrangement rates.

It is not immediately clear how to apply thermodynamics or statistical mechanics to these classes of supercooled systems. One approach consists

in dividing the variables, used to describe the microscopic state, into two groups,  $\{C\}$  and  $\{T\}$ . The first group comprises the instantaneously frozen variables, namely those that specify the atomic sites, but do not contribute to thermal motion, whereas the  $\{T\}$  variables are necessary to describe the thermal motions, such as vibrations and alignment.

$p\{C\}$  is the probability factor that the variables in the set  $\{C\}$  will take on certain values and it is imposed a priori. It describes the system and depends on the method chosen to prepare it. For each  $\{C\}$  we can calculate any thermodynamic quantity using the  $\{T\}$  variables. The quantity under examination is then turned into an average over the distribution  $p\{C\}$  of the frozen variables.



<http://www.springer.com/978-3-540-29609-6>

Disordered Materials

An Introduction

Ossi, P.M.

2006, XII, 329 p. 210 illus., Hardcover

ISBN: 978-3-540-29609-6