2. Variety in Structures

In this chapter we discuss the structure of some of the important phases of condensed matter, including the recently discovered quasicrystalline phase. The focus will be on the symmetry and geometry of the structure concerned, and on the positional correlations of the atoms in it.

2.1 Crystals

A crystal represents a regular arrangement of atoms which can be generated by periodic translations of a basic motif or building block, the unit cell. The symmetry of a crystal is described by its space group. In three dimensions there are 230 space groups, representing the different possible combinations of point-group symmetry and translational symmetry. It is a standard result of crystallography that only certain rotational symmetries are consistent with translational periodicity. These are the so-called crystallographic point groups, of which there are 32.

A crystal has both symmetry and order. Order in the spatial arrangement of atoms is customarily characterized in terms of suitable correlation functions. Let \( \psi(r) \) denote a quantity associated with the atomic arrangement at the point \( r \). Then the correlation function

\[
G_{\psi}(r) = \langle \psi(0) \psi(r) \rangle
\]

(2.1)
describes the spatial correlations of \( \psi \). Here \( \langle \ldots \ldots \ldots \rangle \) denotes a thermodynamic average. In nonmagnetic systems, one is usually interested in the positional correlations of the atoms as described by

\[
G(r) = \langle \rho(0) \rho(r) \rangle
\]

(2.2)

where \( \rho \) denotes the density. The function \( G(r) \) is useful for exploring translational order.

Sometimes one is interested in the orientationally-averaged correlation function

\[
G(r) = \frac{1}{4\pi} \int d\Omega \ G(r)
\]

(2.3)
Here $d\Omega$ is an element of solid angle in $r$-space. The quantity $G(r)$ is sometimes referred to as the radial correlation function. The radial distribution function is

$$P(r) = 4\pi r^2 G(r) .$$

(2.4)

In addition to translational order, one is often interested also in the orientational order. This is studied by means of the orientational correlation functions

$$G_n(r) = \langle Q_n(0) Q_n(r) \rangle$$

(2.5)

where $Q_n(r)$ is a suitably defined quantity characteristic of the interatomic bond centred at $r$ (examples will be given below).

Long-range order (LRO) in $\psi$ is said to exist when

$$\lim_{r \to \infty} \langle (\psi(0) - \langle \psi \rangle)(\psi(r) - \langle \psi \rangle) \rangle \neq 0 .$$

(2.6)

On the other hand, if the correlation function in (2.6) decays to zero as $r \to \infty$, then there is only short-range order (SRO). Crystals have both translational as well as orientational LRO. This statement is strictly true only in three dimensions (3D). In 2D the situation is somewhat different as we shall see in the next chapter.

### 2.2 Incommensurate and Long-Period Structures

A signature of the periodicity of a crystal is the periodicity of its diffraction spots. In recent years, many systems have been discovered for which the diffraction spots are accompanied by satellite reflections. It is now recognised that these satellites are due to certain periodic modulations which exist in the system. As a simple example, consider a 1D lattice (Fig. 2.1a) with sites

$$x_n = an ,$$

(2.7)

where $a$ is the lattice spacing and $n$ is an integer. If the atoms are displaced to new positions $X_n$ defined by

$$X_n = x_n + f \sin(q x_n) \quad q = q_1(2\pi/a) ,$$

(2.8)

then a modulated structure results. If $q_1$ is a nonzero rational number, then the structure (2.8) is also periodic, but with a larger unit cell (Fig. 2.1b). Such a structure is referred to as a commensurate or a long-period structure. When $q_1$ is irrational, there is no periodicity whatsoever, and one has an incommensurate structure (Fig. 2.1c). Although an incommensurate structure lacks periodicity, it has quasiperiodicity, a concept to which we shall return later.