# Structural Coherence in the Condensed State

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## INTRODUCTION

Research in theoretical solid-state physics began long ago with the study of perfect crystals—a study which yielded many important results and which necessarily provides a background for more recent investigations of various defects in crystal structures. These topics are far from being exhausted, from either a fundamental or a practical point of view, but the attention of many solid-state physicists has turned in recent years to the study of liquids and amorphous solids. It is my purpose in this paper to develop the concept of structural coherence in such a way that it can be applied to discussions of the condensed state in any of these forms by concentrating on their similarities rather than their differences.

The idea of structural coherence, though perhaps not given this title, is not a new one and has been used qualitatively in various forms by many workers. What is, I hope, novel is its formalization in the way I intend here. With this in mind I shall not attempt to survey the literature in the field but simply mention those few papers in which my earlier ideas on this subject were developed.

Before giving any formal exposition it is useful to have in mind just what it is that we are talking about. A perfect crystal is certainly structurally coherent in the sense that the unit cells are precisely arranged in a space lattice and the atomic arrangement within each cell is identical. If the crystal structure is a simple Bravais lattice then the environment of each atom is identical in geometry and orientation so that knowledge of this environment for any given atom allows us to extend the structure to infinity in all directions—the structural coherence length is infinite. Similar coherence exists in more complex crystal structures, though we may now have more than one class of atom in the unit cell, distinguished by geometrical environment, chemical nature, or some other property.

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At the other end of the scale we have dilute monatomic gases in which, except for a small exclusion volume, the environment of each atom is determined in a completely statistical manner. In this case the coherence length, depending upon its exact definition, should be taken either as zero or else as equal to the radius of the exclusion sphere around each atom.

Since we are concerned here only with the condensed state, our extreme example should probably be that of a monatomic simple liquid. Such a liquid has, we know, an average co-ordination number of about 10, while the radial distribution function shows structural peaks and valleys out to several times the atomic radius. Presumably structural coherence, however it is defined, has a characteristic decay length of similar magnitude.

As intermediate cases we might consider a polycrystalline solid, for which the structural coherence length is presumably approximately equal to the average crystallite radius, and the more complex case of a single crystal of a disordered alloy such as beta-brass, in which the coherence length for geometrical structure is infinite while that relating to an index of chemical identity is small, corresponding to the decay length for short-range order.

## CORRELATION FUNCTIONS

Since we are concerned with three-dimensional structures and possibly with parameters other than purely geometrical ones, our formalism must take this into account. Our basic concept is that of the generalized four-body correlation function

$$g_4(\mathbf{r}, \mathbf{x} : \mathbf{r}_0, \mathbf{x}_0; \mathbf{r}_1, \mathbf{x}_1; \mathbf{r}_2, \mathbf{x}_2) \tag{1}$$

which is the probability density of finding an atom having attributes $\mathbf{x}$ at position $\mathbf{r}$, given that there are atoms with attributes $\mathbf{x}_i$ at positions $\mathbf{r}_i$ for $i = 0, 1, 2$. We shall concern ourselves in general only with the compact form of $g_4$ in which atoms 1 and 2 are both close neighbours of the atom 0 (which we take to lie at the origin so that $\mathbf{r}_0 = 0$) and such that atoms 0, 1, 2 are not collinear.

We now need to settle one or two other procedural questions about the definition of $g_4$ before we can go on. We can easily choose as our origin $\mathbf{r}_0 = 0$ an atom with attributes $\mathbf{x}_0$ and we can rotate our co-ordinate system so that there is a near-neighbour atom in the direction of $\mathbf{r}_1$. In a crystal, however, such a near-neighbour atom occurs only at a closely fixed distance $r_1$ while in a liquid the distances are spread over a range of $r_1$ corresponding to the loosely-defined nearest-neighbour shell. Let us agree that $g_4$ will consist of a weighted average of the results computed for all possible $r_1$ values within this range.

When we come to atom 2 the situation is similar. We can use the as yet

undefined freedom of rotation of our co-ordinate system about the $\mathbf{r}_1$ direction to choose the plane defined by $\mathbf{r}_1, \mathbf{r}_2$ to pass through another atom of the nearest-neighbour shell. Once again there are limitations on the magnitude $r_1$ and also on the angle between $\mathbf{r}_1$ and $\mathbf{r}_2$ for which an atom can be found. Again we agree to take a weighted average over these values.

The same situation applies to the subsidiary parameters $\mathbf{x}$. For a simple monatomic material these can only refer to geometrical attributes like position in the unit cell—for a diamond cubic structure, for example, there are two non-equivalent atoms in the unit cell so that $\mathbf{x}$ might be assigned the two values $\pm 1$, while for a primitive lattice like face-centred cubic the $\mathbf{x}$ parameter would have the same value for all atoms. For an alloy like brass $\mathbf{x}$ might be taken as $+1$ for copper and $-1$ for zinc atoms. For a complex material like ice or water with the molecules treated as atoms from a geometrical point of view, $\mathbf{x}$ might be a vector quantity specifying the orientation of the electrical dipole of the molecule. In such cases we shall also usually assume that the values of the $\mathbf{x}_i$ to be used in $g_4$ are weighted averages of the accessible values of $\mathbf{x}$, though for some purposes we may wish to concentrate on a particular $\mathbf{x}_i$ assignment.

Finally we must assume that $g_4$ represents an ensemble average over all possible choices of the spatial origin $\mathbf{r}_0$, with the directions of $\mathbf{r}_1$ and $\mathbf{r}_2$ being adjusted for each different choice of $\mathbf{r}_0$ as described above. The parameter $\mathbf{x}_0$ will not generally be included in the ensemble average, so that several different $g_4$ functions may arise for different assignments of $\mathbf{x}_0$.

Correlation functions as complex as $g_4$ are rarely discussed in detail in structural theory but the properties of the related simpler functions $g_3$ and $g_2$, usually without the additional parameters $\mathbf{x}_i$, have been extensively studied. In particular the two-body correlation function $g_2(\mathbf{r} : \mathbf{r}_0)$ is simply related to the radial distribution function $g(r)$ by

$$g_2(\mathbf{r} : 0) = ng(r) \tag{2}$$

where $n$ is the number density of atoms in the condensed state considered. For simple monatomic liquids like argon or sodium or for monatomic solids with primitive lattice structures the 'superposition approximation', which for our particular definition of $g_n$ has the form

$$g_3(\mathbf{r} : \mathbf{r}_0 ; \mathbf{r}_1) \approx n^{-1} g_2(\mathbf{r} : \mathbf{r}_0) g_2(\mathbf{r} : \mathbf{r}_1) \tag{3}$$

is quite well satisfied, at least for the nearest-neighbour shell. This is, however, very far from being true for crystals like diamond with more than one atom per unit cell, for solids like amorphous germanium, or for structured liquids like water. Much of the individuality of these materials and many of their practically important qualities arise from the deviations of $g_3$ from the form predicted by the superposition approximation. Each

of the materials mentioned has at least an approximately tetrahedral atomic environment and therefore effectively two atoms per unit cell or, if we use our extended formalism, two $\mathbf{x}$ values.

Fortunately when we come to consider $g_4$ it seems a reasonable approximation on geometrical grounds, at least for the nearest-neighbour shell, to write

$$g_4(\mathbf{r} : \mathbf{r}_0; \mathbf{r}_1; \mathbf{r}_2) \approx' g_3(\mathbf{r} : \mathbf{r}_0; \mathbf{r}_1) g_3(\mathbf{r} : \mathbf{r}_0; \mathbf{r}_2)/g_2(\mathbf{r} : \mathbf{r}_0) \tag{4}$$

and it is probable that this relation is satisfied also for the more general functions involving the $\mathbf{x}_i$.

Of these correlation functions only $g_2$ can be derived directly from diffraction experiments on liquids or amorphous solids. It is therefore generally necessary, in our present state of knowledge, to deduce information about $g_3$ and $g_4$ from structural models of the liquid. Such models are themselves generally derived from structural information about the bonding pattern of individual atoms or molecules, which thus incorporate information about $g_4$ quite directly. For crystalline solids, of course diffraction experiments provide complete structural information and therefore define the $g_n$ of all orders.

## COHERENCE LENGTH

Before proceeding to a formal definition of coherence length, let us examine the behaviour of $g_4$ for several typical cases. For a perfect crystal at absolute zero, neglecting zero-point vibrations, $g_4$ consists of an array of delta function peaks with the same geometry as the crystal structure. If we remove the delta function nature of the peaks by allowing each atom to vibrate thermally about its ideal lattice position, then the peak height becomes finite (except for a delta function at the origin, which we agree to omit) and the envelope of the peak heights, plotted as a function of radial distance $r$, is a straight line like A in Fig. 1. However we define it in detail, the coherence length in this case is clearly infinite.

If we now introduce a random set of dislocations into the crystal, it is apparent that when the ensemble average over positions of the origin implied in the definition of $g_4$ is taken, peaks at radial distances greater than the average spacing between dislocations tend to be displaced through distances related to the Burgers' vectors of the dislocations. The actual displacement depends on the geometrical relation between $r$ and the dislocation line, so that ensemble averaging effectively blurs out the more distant peaks in $g_4$. An envelope curve through the tops of these peaks therefore has a form like B in Fig. 1. The curve behaves rather like $\exp(-r/\ell)$, where the characteristic length $\ell$ is of the order of the distance between dislocations.

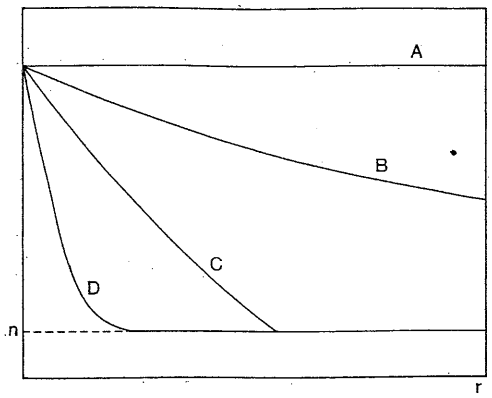


FIG. 1. Envelope of peak heights $g_4$ (omitting the delta-function peak at the origin) for (A) a perfect crystal, (B) a crystal contaning dislocations (C) a polycrystalline material, and (D) a liquid or vitreous solid. In each case $n$ is the number density of the atoms.

A polycrystalline solid with average crystallite diameter $d$ clearly has a $g_4$ function which assumes the uniform value $n$, equal to the number density of atoms, for all $r$ greater than about $d$, and so has the form of curve C in Fig. 1. If however, the crystal is of ideal mosaic form so that the orientations of all the crystallites are closely clustered about some common orientation, there will be no sharp corner as in curve C but rather a quasi-exponential decay towards $n$ for $r$ greater than $d$. Crystalline solids can, of course, exhibit texture effects so that the curves A, B, C might well differ in their length scale for different directions in the sample, but we neglect this complication.

Finally we consider the case of a liquid. Quite clearly the randomness of the structure means that the peak heights fall off very rapidly with distance but we need to see how to calculate $g_4$ for such random structures. In the case of a simple liquid to which the superposition approximation of eqn. (3) applies, we see from eqn. (4) that, at least for the nearest-neighbour shell,

$$g_4(\mathbf{r} : \mathbf{r}_0; \mathbf{r}_1; \mathbf{r}_2) \approx n^{-2} g_2(\mathbf{r} : \mathbf{r}_0) g_2(\mathbf{r} : \mathbf{r}_1) g_2(\mathbf{r} : \mathbf{r}_2). \tag{5}$$

As far as the nearest-neighbour shell is concerned $g_2(\mathbf{r} : \mathbf{r}_i)$ amounts to a spherically symmetric shell centred on $\mathbf{r}_i$ and having a more or less Gaussian radial profile corresponding to the first hump in the radial distribution function $g(r)$. $g_4$ is then the intersection of three such spherical shells centred on the points $\mathbf{r}_0$, $\mathbf{r}_1$ and $\mathbf{r}_2$. It consists, as far as the atom positions which are nearest neighbours to the points $\mathbf{r}_0$, $\mathbf{r}_1$ and $\mathbf{r}_2$ are concerned, of a pair of ellipsoidal probability maxima. These maxima are not spherical because we must take into account the distribution in

the length of $\mathbf{r}_1$ and $\mathbf{r}_2$ and of $\mathbf{r}_1 - \mathbf{r}_2$ by adding the variances of the Gaussian distributions in the appropriate directions. The standard deviations associated with the ellipsoid are thus between 1 and about 1.6 times those of the peak in $g(r)$.

This is not yet enough to define $g_4$ since we must construct the entire neighbourhood of the atom at $\mathbf{r}_0$ and then perform an ensemble average. To do this, we first complete the nearest neighbour shell of $\mathbf{r}_0$ by continuation of the process outlined above remembering that when one of the basis atoms (equivalent to $\mathbf{r}_1$ and $\mathbf{r}_2$ in the first step above) has a probability distribution as a result of the step generating it, this distribution must be compounded with the Gaussian width of $g(r)$ by adding the variances.

Having completed the nearest-neighbour shell of $\mathbf{r}_0$ in this way, the probability peaks becoming broader and lower as we proceed further away from the original reference atoms at $\mathbf{r}_1$ and $\mathbf{r}_2$, we then go on to construct the next-neighbour shell of $\mathbf{r}_0$ in a similar way. We stop only when the probability peaks become wide enough that their overlap leads to an essentially constant probability density. Finally we plot the average height of probability peaks as a function of distance from the reference atom at $\mathbf{r}_0$ to obtain a curve like D in Fig. 1. Incidentally, if we plot not the peak height but rather the average probability density as a function of distance, we should regain the radial distribution function $g(r)$.

For a structured liquid like water or a glassy solid like amorphous germanium, in which cases the superposition approximation of eqn. (3) is not even approximately valid, we usually begin either with a knowledge of $g_4$ or at least of $g_2$ and $g_3$, from which $g_4$ can be found from eqn. (4). Typically this information might be contained in a statement about the approximate symmetry of the environment (e.g. tetrahedral), the distribution of nearest-neighbour distances (or bond lengths) and the distribution of nearest-neighbour angles about the values prescribed by symmetry. From such information, which must of course be consistent with the observed radial distribution function, we can proceed very much as before to extend the probability distribution over the whole neighbourhood and hence to determine a curve like D of Fig. 1. Pople's model for liquid water is of this form (1).

In some cases the model description of the vitreous or liquid state may, however, be very different. This is so for the various 'cluster' models for liquid water in contrast with a uniform 'bond-distortion' model of the type mentioned above. Such cluster models generally idealize the liquid as a mixture of several significant structures of specified size distribution. For example water may be pictured as clusters of about 50 molecules in ice-like bonding configuration dispersed in a simple liquid of unbonded molecules (1). When the model is as specific as this, it is relatively simple

to estimate the behaviour of $g_4$ with distance, the characteristic decay length being of the order of the radius of the clusters. For water near 0°C both the distorted-bond model and the cluster model agree in giving a coherence length close to 1 nm.

From this discussion it is clear that a useful definition of structural coherence length can be formulated by plotting the average peak height of $g_4$ as a function of $r$, making a mean-square fit of an exponential function $A \exp(-r/\ell)$, and defining $\ell$ to be the structural coherence length. An exactly analogous definition can be used if we are concerned with one of the other parameters $\mathbf{x}$ instead of simply with position.

Representative calculations show that the structural coherence length can vary from about 10 mm for high quality single crystals of germanium or silicon, through perhaps 0.1 mm for finely polycrystalline metals and 0.01 mm for heavily cold-worked metals to less than 1 nm for liquids and vitreous solids. Other parameters, such as dipole orientation in ice or water, may have similar coherence lengths (less than 1 nm) in both liquid and crystalline phases, while the chemical ordering parameter in a crystal can have a coherence length of order 1 nm above the ordering temperature but as large as 1 mm below this temperature. Clearly co-operative phenomena have an immense effect upon coherence.

## APPLICATIONS

As set out above, the notion of structural coherence, with which is associated a characteristic length or a particular parameter in a particular material, is formally attractive but has no very obvious applications. In the following paragraph I will examine several ways in which the concept has proved fruitful.

### *Band Structure of Liquids* (2)

An important question some years ago was to understand why it is that amorphous germanium or silicon films prepared by condensation onto a cold substrate exhibit semiconducting properties very similar to those of single crystals of the same materials whereas the liquid elements behave as metallic conductors. We give in outline an argument which provides at least a partial answer to this problem.

Crystalline germanium has a diamond cubic structure so that each atom has a tetrahedral environment and there are two non-eqiuvalent atoms in the primitive unit cell. In a tight-binding approximation to the calculation of band structure the orbitals of each atom are hybridized to tetrahedral $sp^3$ configuration and the valence band consists of combinations of orbitals with opposite signs on the two non-equivalent atoms. The conduction band states, separated from those of the valence band by

an energy gap, are formed from orbitals with the same sign on each of the non-equivalent atoms.

The discussion to which we refer examines a two-dimensional analog of this situation in which each atom has three nearest neighbours and the non-equivalent atoms are related by a rotation through 60°. In the analysis it is shown that a band gap (the essential feature of a semiconductor) persists provided the uncertainty in angular orientation (due to bond distortion) between nearest neighbours is substantially less than 30°. Once the uncertainty exceeds 30° the atoms are no longer non-equivalent, the whole character of the electron wave function changes, and the band gap disappears. The differences in short-range order between the vitreous solid and the melt are enough to account for this distinction.

In terms of our present discussion we can deal either with the geometrical structure itself or we can introduce a new parameter $\mathbf{x}$ taking on the values $+1$ or $-1$ according as the bond orientation of an atom conforms in some mean-square way to one or other of the ideal crystalline orientations. In either case if the coherence length is much larger than the nearest-neighbour spacing the material tends to exhibit a band gap, while if it is comparable with or smaller than the interatomic spacing metallic properties result.

*Surface Structure of Water and Ice* (3)

This is the first of a series of problems in which we are concerned not with the breakdown of structural coherence away from an atom at the origin but rather with its breakdown away from a plane surface. It is easy to see in a general way that the structural coherence length in this second case is usually a good deal larger than in the first. The main reason is that the initial condition, whatever it is, is established for essentially all the atoms of a plane, so that the atoms of the next layer are all similarly influenced by several neighbours in this plane rather than simply by a single atom at the origin. The breakdown of structural coherence is thus rather analogous to a process of diffusion which follows a law like $\exp(-z/\ell)$ in the one-dimensional case but the appreciably steeper law $(1/r)\exp(-r/\ell)$ in the spherically symmetric case.

Again we give the argument in outline and expressed in terms of our present discussion. Because the water molecule is not a symmetrical dipole but possesses large quadrupole moments, molecules at the interface between liquid water and vapour have a preferred orientation, probably with their protons directed into the liquid. It turns out that, using dipole orientation as our structural parameter $\mathbf{x}$, the one-dimensional coherence length for liquid water near 0°C is about 1 nm or three molecular layers, so that any preferred orientation induced at the surface extends into the liquid for about this distance. Particular conse-

quences follow in relation, for example, to surface potential and surface electrical conductivity.

In the case of a single crystal of ice a similar surface orientation is energetically preferred but, because the one-dimensional coherence length for decay of orientation is of the order of 1 mm in a single crystal of ice, entropy penalties preclude surface orientation.

If, however, the temperature is close to the melting point, it seems possible to lower the free energy of the whole system by melting a thin layer at the surface in order to take advantage of both the short coherence length of liquid water and the possibility this allows for surface orientation. Order-of-magnitude calculations suggest a liquid film thickness of about 10 nm at $-1°C$, varying roughly inversely with the temperature depression below the melting point. While this rather speculative theory has yet to be unambiguously confirmed, there is a certain amount of persuasive evidence in its favour.

*The Solid–Liquid Interface* (4)

As a final example let us consider the structure and dynamics of the interface between a crystal and its melt. Clearly the crystal provides a well defined set of atomic positions which constrain the configuration of the neighbouring liquid structure in a rather more rigorous and compatible way than would the atoms of another solid. If we are provided with information about $g_4$ or, equivalently, with a structural model for the liquid, we can calculate the structural diffusion length in a direction normal to the interface. Typically it is about 1 to 2 nm and significantly greater than the normal spherical coherence length.

Within a distance of order one coherence length from the interface, the structure of the liquid is more 'crystalline' than in bulk liquid and it has both a lower energy and a lower entropy than the bulk. Calculations suggest that the entropy contribution is dominant and that it is this which largely accounts for the measured solid–liquid interfacial free energy. This conclusion leads to the further prediction that the interfacial free energy should decrease with decreasing temperature, a prediction which is in general accord with experiment. The numerical values derived from the theory are also in moderately good agreement with experiment for the few cases that have been studied.

When we turn to examine the kinetic problem of crystal growth from the melt, we recognise that the structural modification of the liquid near the interface must propagate through the liquid with the same velocity as the growing crystal and that this necessarily involves structural diffusion in the liquid. Analysis of this situation shows that there are two possible crystal growth regimes. If the coherence length in the liquid is a good deal larger than the interatomic spacing, then there is effectively no

free energy barrier to interface motion and we have the familiar situation usually thought of as continuous growth with a rough interface. On the other hand, if the coherence length is comparable with the interatomic spacing, a significant free energy barrier prevents interface advance. This corresponds to the situation with a smooth interface, when a two-dimensional nucleation process or a screw dislocation mechanism must be invoked to avoid the free energy barrier. More detailed analysis of the kinetics of the situation also allows prediction of the concentration of imperfections included in the crystal during the growth process, as a function of crystallization velocity.

## CONCLUSION

It has been impossible in this short survey to do more than outline the possible basis for a unified treatment of some aspects of the physics of the condensed state which seems to offer a new approach to some old problems. The formalism of the method exists as yet only in an embryonic state and it will not be an easy task to develop it precisely. The interest of the semi-quantitative treatments of problems to which it has so far been applied, however, suggests that the effort may be worthwhile.

## REFERENCES

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