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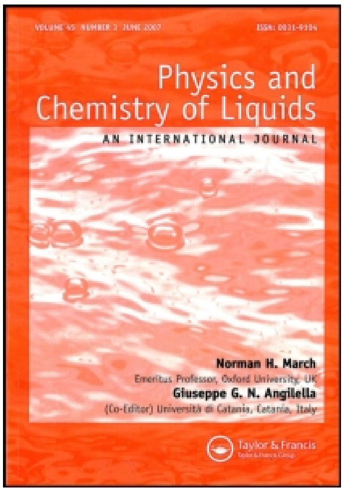

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Information Content of Diffraction Experiments on Liquids and Amorphous Solids

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REVIEW ARTICLE
Information Content of Diffraction Experiments on Liquids and Amorphous Solids

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Starting with simple monatomic liquids such as condensed rare gases, the information that can be extracted from diffraction experiments is discussed. The rich interplay between atomic and electronic structure in liquid metals such as Na and K is emphasized: expanded Rb and Cs taken up the liquid–vapour coexistence curve towards the critical point are also mentioned. A liquid metal like Na is, in fact, a two-component system, Na^+ and electrons. Classical two-component systems are also considered, and specifically $BaCl_2$ which freezes into a fast-ion conducting phase. The structural theory of two-component liquids is extended to apply to amorphous Si, the 'second component' now being the bond charge. The way a combination of X-ray and electron diffraction can elucidate the nature of the local ordering, as well as the directional bonding, is stressed. There is clear evidence here for the bonding electrons, directly from the X-ray and electron scattering intensity.

KEY WORDS: Partial structure factors, directional bonding

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1 INTRODUCTION

That the short-range order existing in liquids such as condensed rare gases could be extracted from X-ray diffraction experiments has been known for a long time. If we write the intensity I of X-rays of wavelength λ scattered through an angle 2Θ by a liquid sample containing N atoms:

$$I(k) = Nf^2(k)S(k) : k = \frac{4\pi \sin \Theta}{\lambda} \tag{1.1}$$

then $S(k)$ is the liquid structure factor, related to the pair correlation function $g(r)$ by

$$S(k) = 1 + \rho \int [g(r) - 1] \exp(i\mathbf{k} \cdot \mathbf{r}) d\mathbf{r}, \tag{1.2}$$

with ρ the atomic number density. If one considers neutron rather than X-ray diffraction, then the atomic scattering factor $f(k)$ in Eq. (1.1) is replaced by a k independent neutron scattering length.

It is fair to say that all simple liquids near their triple point have remarkably similar forms of $S(k)$ and $g(r)$. In one sense, this is disappointing, as a hard sphere model can account for a lot of features. However, on closer inspection, departures from hard spheres become apparent and, we shall argue, it is these departures that are the matters of most interest for the chemical physics of condensed matter.

In Section 2 therefore, we shall summarize what we can learn from $S(k)$ measurements, taking as prototypes Ar and Na. Here theory is now relatively well developed, for such one-component liquids. Actually, in Section 5 we shall return to liquid Na, with some surprises to follow!

Section 3 then takes two examples of ionic melts: RbCl and $BaCl_2$, the latter, in the crystalline phase, being a fast-ion conductor: these also serve to introduce the structural description of two-component systems.

The other examples both involve electrons in disordered systems: probed directly by X-rays, and also usefully by electron diffraction. Cases treated are SiO_2 and amorphous Si in Section 4, and also in Section 5, as already remarked, liquid Na. Section 6 discusses some promising future directions for experiment and theory.

2 STRUCTURE AND FORCES IN SIMPLE MONATOMIC LIQUIDS NEAR TRIPLE POINT: e.g. Ar and Na

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One can usefully group properties that are expected to arise in $S(k)$ and $g(r)$ according to first-principles liquid-state theory into three areas.

2.1 Small angle scattering

For van der Waals liquids such as Ar, the pair potential $\phi(r)$ at large r is expected to take the (non-retarded) form

$$\phi(r) = -\frac{c_6}{r^6} \tag{2.1}$$

This was shown by Enderby, Gaskell and March[1] to lead to a small k expansion of the structure factor $S(k)$ of the form

$$S(k) = S(0) + a_2k^2 + a_3k^3 + \cdots \tag{2.2}$$

From the theoretical result (true far from the critical point) that at sufficiently large r the Ornstein–Zernike direct correlation function $c(r)$ reflects the pair potential $\phi(r)$ through

$$c(r) = -\frac{\phi(r)}{k_BT}, \; r \text{ large} \tag{2.3}$$

one derives, using (2.1) the result for the coefficient of the k^3 term in Eq. (2.2):

$$a_3 = \pi^2\rho\{S(0)\}^2c_6/12k_BT \tag{2.4}$$

and this result (2.4) has been tested by confrontation with the diffraction experiments of Yarnell[2] *et al.* for argon. The theoretical estimate of c_6 is in good accord with that extracted from Eq. (2.2): the work of Robinson and March[3] (see also Renne and Nijboer[4]) showing that a few percent reduction only in c_6 is to be expected because of the van der Waals interactions taking place in a dielectric liquid. The situation in liquid metals is more complex and is not accounted for by Eq. (2.2), as discussed by Matthai and March[5].

2.2 *Freezing and melting criteria*

The second feature we focus on is the so-called Verlet rule[6], that $S(k)$, as we cool down the liquid, approaches a maximum value at its principal peak of about 2.8, before freezing occurs. This, found by Verlet for Lennard-Jones liquids, also holds for simple metals, which, as pointed out by Ferraz and March[7], are usefully described around the principle peak by the classical one-component plasma model (OCP). This OCP freezes when $S(k)$ reaches a maximum of about 2.7, in accord with the X-ray experiments of Greenfield, Wellendorf and Wiser[8] on liquid Na and K near the melting temperature T_m. Bhatia and March[9] have shown that:

i) There is no conflict between the Verlet rule for freezing and the Lindemann law for melting, which in turn relates to

ii) The result, derived from the condition $g(r = 0) = 0$ in dense classical liquids:

$$S(k)_{\max} \doteq \frac{3}{8}\frac{k_{\max}}{\Delta k} \tag{2.5}$$

where $2\Delta k$ is the distance between the two adjacent nodes of $S(k) - 1$ embracing the principal peak. Silbert (private communication) has verified the approximate validity of Eq. (2.5) above from diffraction data on wide range of liquids.

2.3 *Inverse problem of extracting forces from measured structures*

An attractive possibility, pointed out some 25 years ago by Johnson and March[10], is to extract the entire pair potential $\phi(r)$ directly from diffraction measurements of $S(k)$. Their work is taken, nowadays, to define the 'inverse problem' of extracting forces from structure. This has recently been brought to fruition, especially by Levesque, Reatto and Weis[11] and also by Dharma-wardana and Aers[12] (for a fuller review, see March[13]). The idea is simply expressed. If we write, for a classical liquid $g(r)$ in the Boltzmann form

$$g(r_{12}) = \exp\left(-\frac{U(r_{12})}{k_B T}\right), \tag{2.6}$$

then the potential of mean force $U(r_{12})$ can be used to construct the total force $-\partial U(r_{12})/\partial \mathbf{r}_1$ acting for atom 1. In turn, this arises from the sum of the pair force $-\partial\phi(\mathbf{r}_{12})/\partial\mathbf{r}_1$ exerted by atom 2 at separation r_{12}, and the contribution from the other atoms. Thus, we can write

$$-\frac{\partial U(r_{12})}{\partial \mathbf{r}_1} = -\frac{\partial\phi(r_{12})}{\partial \mathbf{r}_1} - \rho\int \frac{g^{(3)}(\mathbf{r}_1\mathbf{r}_2\mathbf{r}_3)}{g(r_{12})}\frac{\partial\phi(r_{13})}{\partial \mathbf{r}_1}\,d\mathbf{r}_3, \tag{2.7}$$

the so-called force equation where the final term in Eq. (2.7) evidently involves the probability $g^{(3)}(\mathbf{r}_1\mathbf{r}_2\mathbf{r}_3)/g(r_{12})$ that a third atom is at $\mathbf{r}_3$ given atoms 1 and 2 at

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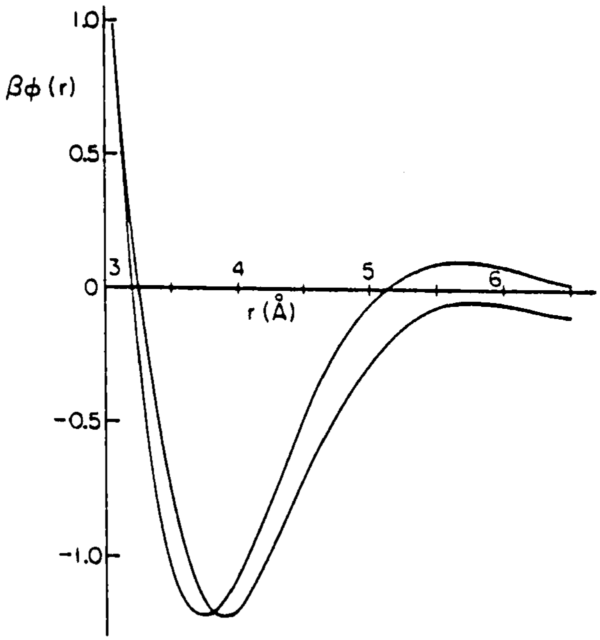

Figure 2.1 Pair potential $\phi(r)$ for liquid Na at melting point T_m in units of $\beta^{-1} = k_B T_m$. Lower curve for larger r is obtained by inversion of structure factor $S(k)$ and is taken from Refs. 11 and 14. Upper curve for large r is electron theory calculation of Perrot and March[14].

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$\mathbf{r}_1$ and $\mathbf{r}_2$. Eq. (2.7) is an exact consequence of classical statistical mechanics for a liquid with pairwise additive forces. Evidently, since U is known from $g(r)$ through Eq. (2.6), $\phi(r)$ can be extracted only if knowledge of $g^{(3)}$ is assumed. By an iterative predictor-corrector technique in which the predictor is the modified hypernetted-chain method, while the corrector is simulation, Levesque, Reatto and Weis have adopted the proposal of Johnson and March and have successfully extracted $\phi(r)$ for Ar from simulation data and Na from diffraction measurements. This procedure is fully reviewed by Reatto[14]: the potential $\phi(r)$ thereby obtained from $S(k)$ for Na liquid near freezing is shown in Figure 2.1

It is worth pointing out that approximate analytical theories are still of considerable interest and these have taken two main directions:

i) Theories leading to

$$U(r) - \phi(r) = \int h(|\mathbf{r} - \mathbf{r}'|)F(\mathbf{r}')d\mathbf{r}', \tag{2.8}$$

which were proposed by the writer[15], and have been developed recently by Gaskell[16], and

ii) A theory, due to Barrat, Hansen and Pastore[17], based not on the Kirkwood decoupling of $g^{(3)}$ as a product of pair functions $g(r_{12})g(r_{23})g(r_{31})$ but of the three-body Ornstein–Zernike function

$$c^{(3)}(\mathbf{r}_1\mathbf{r}_2\mathbf{r}_3) = t(r_{12})t(r_{23})t(r_{31}) \tag{2.9}$$

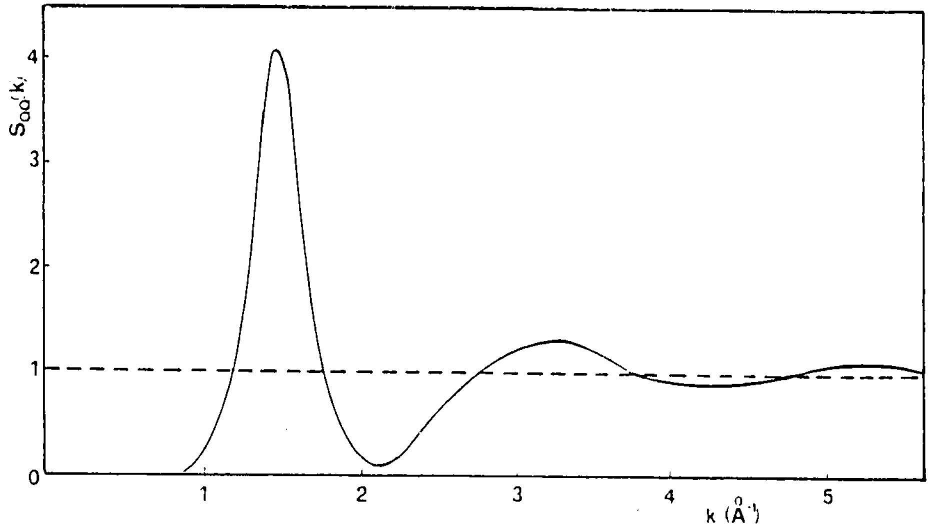

Figure 3.1 Charge–charge structure factor for molten RbCl, constructed from neutron diffraction data on partial structure factors (after March and Tosi[23]).

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Here t is chosen empirically to yield correctly $c^{(3)}$ from the density derivative $\partial c/\partial \rho$. This assumption (2.9) has been considered recently in the context of the inverse problem by March and Senatore[18], though, to date, no numerical results of this approximate theory of the inverse problem are available to the writer's knowledge.

In summary, a great deal of valuable information is contained in measurements of $S(k)$ for liquids near the triple point. In view of the very fine experiments of Jüngst, Knuth and Hensel[19] on the structure factor of Rb and Cs along the coexistence curve of these expanded fluid metals, an extension of the above analysis for extracting $\phi(r)$ will be of considerable interest to study the variation of $\phi(r)$ with thermodynamic state as the metal-insulator transition is approached*. This transition, especially in expanded fluid Na, has technological[20] as well as fundamental interest[21].

3 IONIC MELTS: ESPECIALLY RbCl AND $BaCl_2$

Page and Mika[22] used the technique of isotopic substitution on CuCl to determine the partial structure factors S_{11}, S_{22} and S_{12} of an ionic melt. This same technique is illuminating in showing, in molten alkali halides, the charge ordering known to exist in crystalline NaCl say. The appropriate combination of the corresponding pair functions of g_{11}, g_{22} and g_{12} reflecting the charge–charge (QQ) correlation function is (see, for example, March and Tosi[23])

$$g_{QQ}(r) = g_{11} + g_{22} - 2g_{12} \tag{3.1}$$

and the Fourier transform $S_{QQ}(k)$ for molten RbCl is shown in Figure 3.1.

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* Note added in proof. Preliminary results have now been reported (J. A. Ascough and N. H. March (1990) Phys. Chem. Liquids 21, 251) for a low density metallic state of Cs.

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It is interesting that before the diffraction data on ionic melts became available, many of the important features of the structure factors of the molten alkali halides had been determined by Singer and co-workers[24], by computer simulation, reflecting the better understanding of force fields in these melts than in, say, liquid metals. Biggin and Enderby[25] have discussed at length the meaning of coordination numbers extracted from diffraction experiments. The coordination number is, though slightly ambiguous as these workers emphasize, reduced somewhat on melting.

After this brief introduction to the structure of a two-component liquid, we shall comment in a little more detail on what can be gleaned from partial structure factor measurements on $BaCl_2$. This material is in the class of fast-ion conductors having, in the solid state, the fluorite structure. As March and Tosi[26] have emphasized, the partial structure factors in the liquids already reflect the fact that, on freezing, $BaCl_2$ will have dominant Frenkel defects, in contrast to RbCl with dominant Schottky defects. In other words, liquid structure already, just above the melting temperature, has fingerprints of the defect structure to be expected on freezing.

March and Tosi[27] have given a zero-order theory, related to the work of Ramakrishnan and Yussouff[28] for the freezing of simple liquids such as Ar and Na, for the freezing of $BaCl_2$ into a fast-ion conducting state. Just below the melting point, making admittedly drastic assumptions about the order parameters in $\mathbf{k}$ space, they can characterize the lattice liquid formed by the anions (i.e. liquid in the periodic potential created by the frozen cation sub-lattice) by Fourier components of the density at the first reciprocal lattice vector. This can be related to structure through the admittedly approximate linear response theory to yield

$$\rho_{2G} = \frac{(\rho_{21}/\rho_{11})^{1/2}\tilde{c}_{12}(G)\rho_{1G}}{(\rho_{21}/\rho_{20}) - \tilde{c}_{22}(G)}. \tag{3.2}$$

As was to be expected, the coupling of the cation sub-lattice 1 to the liquid density modulations ρ_{2G} is determined by the Ornstein–Zernike cross-correlation function $\tilde{c}_{12}(G)$. The denominator in Eq. (3.2) represents, in essence, the response function of the system 2, i.e. the anions in $BaCl_2$. ρ_{21} denotes the mean anion singlet density in the liquid phase etc. D'Aguanno *et al.*[29] have subsequently studied this problem numerically and later work of Rovere and Tosi[30] has been concerned with the fast-ion transition itself. However, for some cautionary remarks about the truncation of the sums over reciprocal lattice vectors, see Haymet *et al.*[31], and further work is clearly called for in this area.

4 X-RAY AND ELECTRON SCATTERING FROM DISORDERED SOLIDS

Having introduced the partial structure factors of two-component liquids, with reference to RbCl and $BaCl_2$, we turn to consider diffraction from disordered solids. Again, it will be helpful to do it by examples: we mention here SiO_2[32], amorphous Si[33] and amorphous C[33,34]. While, we believe, the scattering theory outlined below will have more general usefulness, it has been applied most extensively so far to

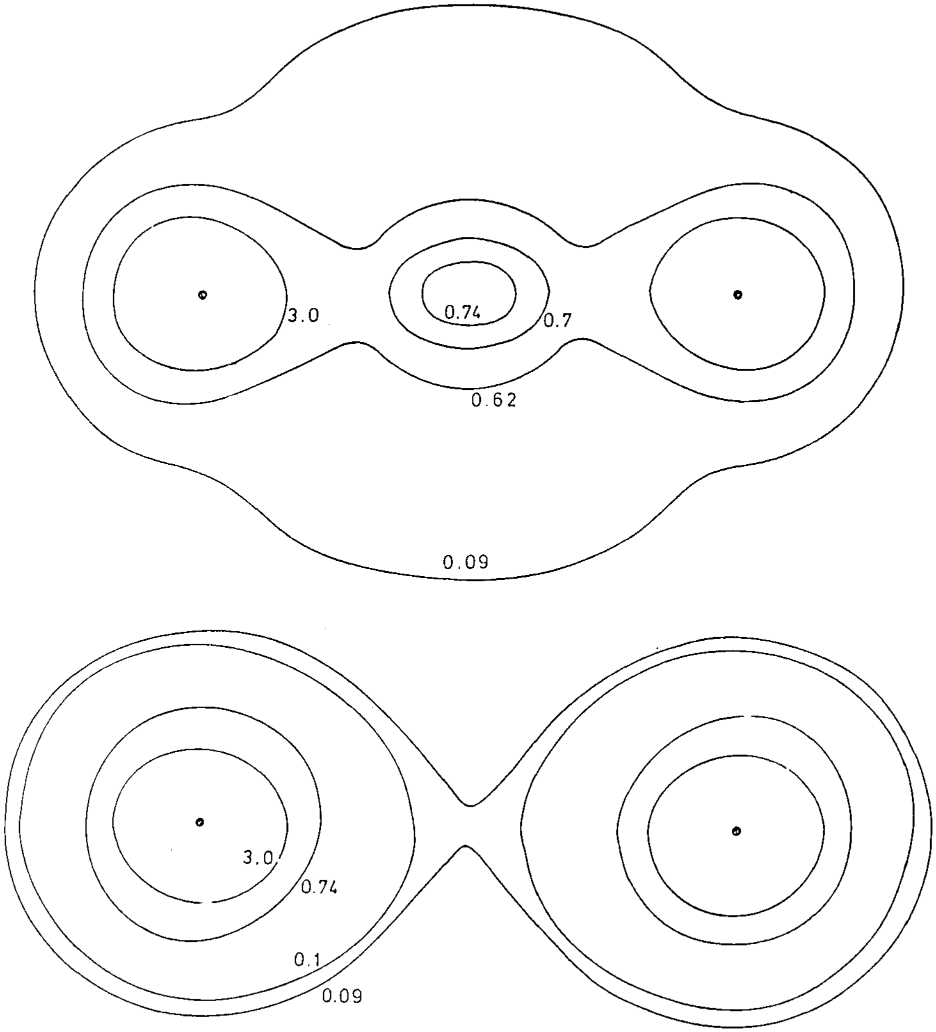

Figure 4.1 Contours of equal electron density for a Si–Si bond as in amorphous Si, starting from sp^3 hybrids built from the 3s and 3p Si atomic wave functions. Linear combination of atomic orbitals (LCAO) method is then employed to construct figure (after Stenhouse *et al.*[33]) (b) Superposition of isolated atom densities for comparison with bond in (a).

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amorphous Si[33], and so we shall focus almost exclusively on this disordered solid. However, to introduce the discussion of amorphous Si, it is relevant to note that the work on SiO_2 constructed the three partial structure factors for vitreous silica from random network models due to Bell and Dean[35]. In addition to the model structure factors thereby obtained, X-ray scattering factors must be specified in order to calculate the X-ray intensity (cf Eq. (4.2) below). In Ref. 32, though it was recognised that chemical bonding should eventually be included explicitly, neutral Si and O atomic scattering factors were employed. It was noted from the work of King[36] that

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the height of the first peak in the X-ray scattering is significantly altered by using instead the scattering factors for Si^{4+} and O^{2-}. Following this brief comment on vitreous silica, we turn to the main example of the section, namely amorphous Si.

Given the nuclear–nuclear pair correlation function $g(r)$ for amorphous Si, one could attempt to use Eq. (1.1) with $f(k)$ replaced by a neutral atomic scattering factor for Si (see Figure 4 of Ref. 33). With a suitable continuous random network (CRN) model for $g(r)$, one calculates $S(k)$ from Eq. (1.2) and hence the X-ray intensity $I_x(k)$. The conclusion is, unambiguously, that the first peak in the X-ray intensity to too low to agree with experiment. When the same CRN model is used to calculate the electron diffraction intensity using[33]

$$I_e(k) = \text{const}\; k^{-4} S(k)[Z - f_{\text{atomic}}(k)]^2, \tag{4.1}$$

then the first peak is too high to agree with experiment.

The reason for the disagreement is not far to seek in qualitative terms. Figure 4.1(a) shows contours of equal electron density for a Si–Si bond as in amorphous Si, starting from atomic sp^3 hybrids built from the 3s and 3p wave functions. Then the linear combination of atomic orbitals (LCAO) method is employed to construct Figure 4.1(a). If we compare these electron density contours with those of Figure 4.1(b), which is merely a superposition of isolated atom densities[33], the marked difference between this superposition density and that of the LCAO density shown in Figure 4.1(a) is the absence in (b) of the closed, almost spherical, contours round the bond centre.

4.1 *Effects of chemical bonding on diffraction intensities*

The LCAO contours indicate that to model the covalent bond one should include, in addition to the superposition of spherical charge clouds on each Si nucleus, a spherical charge distribution at the bond centre, an idea exploited by Phillips[37] and other workers. Whereas Phillips was concerned with dielectric properties and lattice dynamics, and was able to model the bond charge as a point charge, the concern here is modelling diffraction intensities which will evidently require an extended spatial bond charge distribution. Before discussing the form of this, let us emphasize next that this immediately leads to the introduction of a further structural characterization, the bond centre, to supplement $S(k)$ discussed already.

The same CRN model was used therefore to calculate the nuclei-bond centre partial structure factor $S_{nb}(k)$ and the bond centre-bond centre structure factor $S_{bb}(k)$: these, taken from Ref. 33, are shown in Figure 4.2, along with $S(k)$.

Once the scattering factors $f_a(k)$ and $f_b(k)$ of the 'atomic' blobs (f_a) and the bond charge (f_b) are known, then the scattering is as from a two-component liquid and we can write for the X-ray intensity with suitable normalization[33]

$$I_x(k) = f_c^2(k)S(k) + 2f_b^2(k)S_{bb}(k) + 2(S_{nb}(k) - 1)f_c(k)f_b(k) \tag{4.2}$$

with $f_c = 4f_a$.

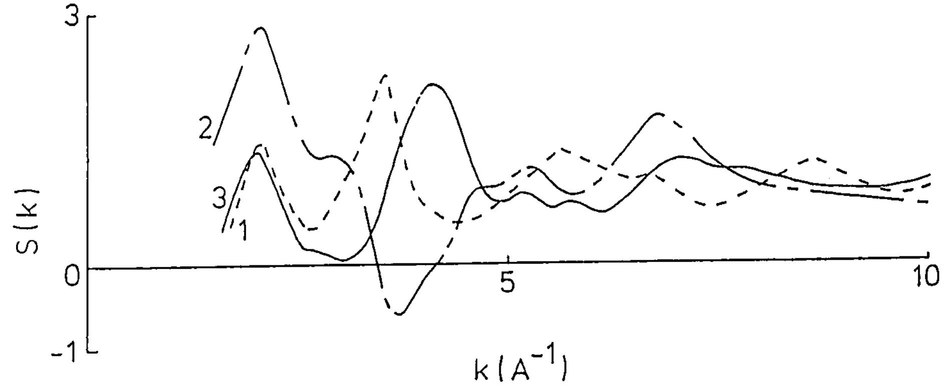

Figure 4.2 Partial structure factors for amorphous Si. (1) $S(k)$ is the nuclear–nuclear structure factor for amorphous Si (2) $S_{nb}(k)$ is nuclei–bond structure factor while (3) $S_{bb}(k)$ is that for bond-centre structure.

Similarly, the electron scattering intensity is given by

$$\begin{aligned} I_e(k) &= \text{const } k^{-4}\{[Z - f_c(k)]^2 S(k) \\ &\quad + 2f_b(k)^2 S_{bb}(k) - 2[S_{nb}(k) - 1][Z - f_c(k)]f_b(k)\}. \end{aligned} \tag{4.3}$$

Putting $f_b = 0$ and $f_c = f_{\text{atomic}}$ in Eq. (4.3), Eq. (4.1) is regained. Equations (4.2) and (4.3) are the basic equations for modelling the diffraction intensities, to allow for the effects of chemical bonding.

The choice of f_a and f_b is fully discussed in Ref. 33, and these form factors are simply plotted in Figure 4.3. These, in turn, lead back to the equal electron density

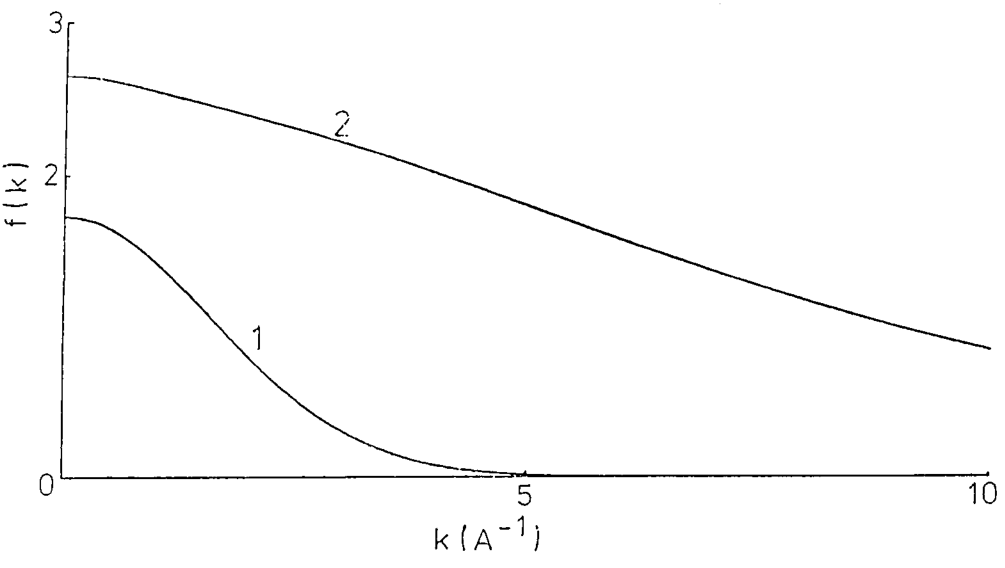

Figure 4.3 Form factors f_a and f_b appearing in intensity Eq. (4.2). f_a(k) is upper curve.

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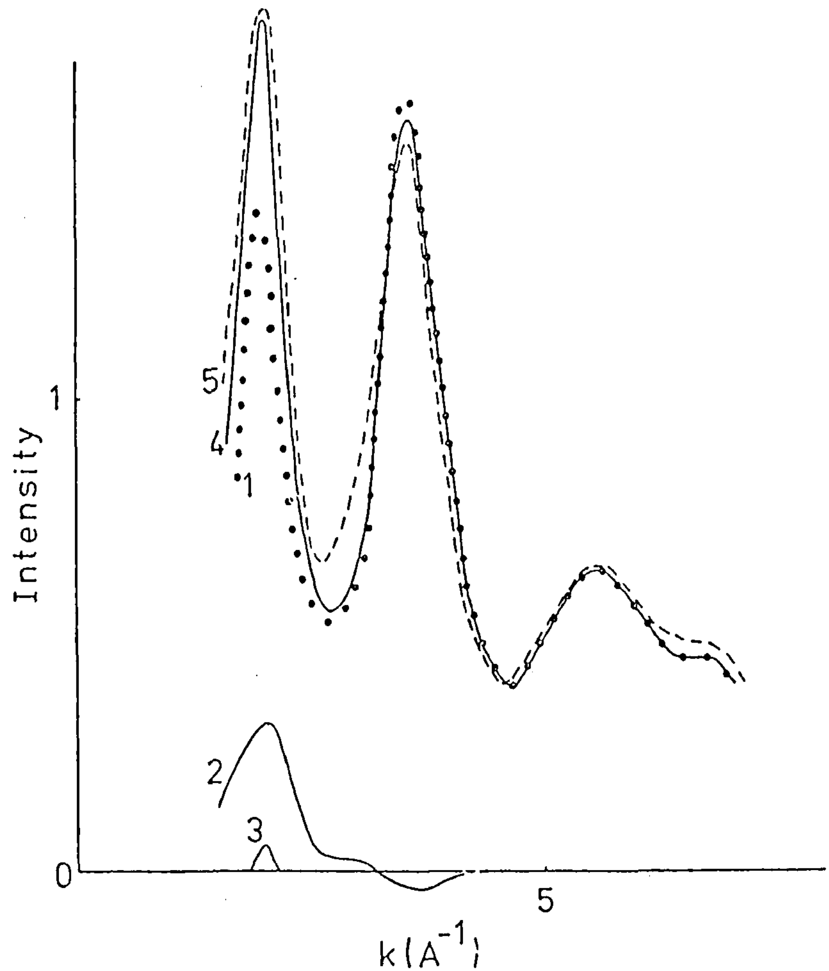

Figure 4.4 X-ray scattering intensity for amorphous silicon, using continuous random network model. (1) Contribution from Si–Si correlations (2) From Si-bond-centre correlations (3) Bond-centre contribution (4) Total predicted intensity (5) Experiment[33].

contours which are practically indistinguishable from those in Figure 4.1(a). Reference to Figures 4.4 and 4.5 show how the inclusion of the bond charge brings theory and experiment into substantial agreement for both X-ray and electron diffraction.

Though, no doubt, some refinements of structure and of electron distribution could now be made, we emphasize in the present context that one can gain confidence in the CRN structural model (with odd membered rings[33]) and in the detailed treatment of chemical bonding. A model built from ordered units turns out to be clearly inferior to the CRN model, while a superposition of spherical blobs on the Si nuclei fails to account for the diffraction intensities. As shown, in fact, in Ref. 33, use of the bond

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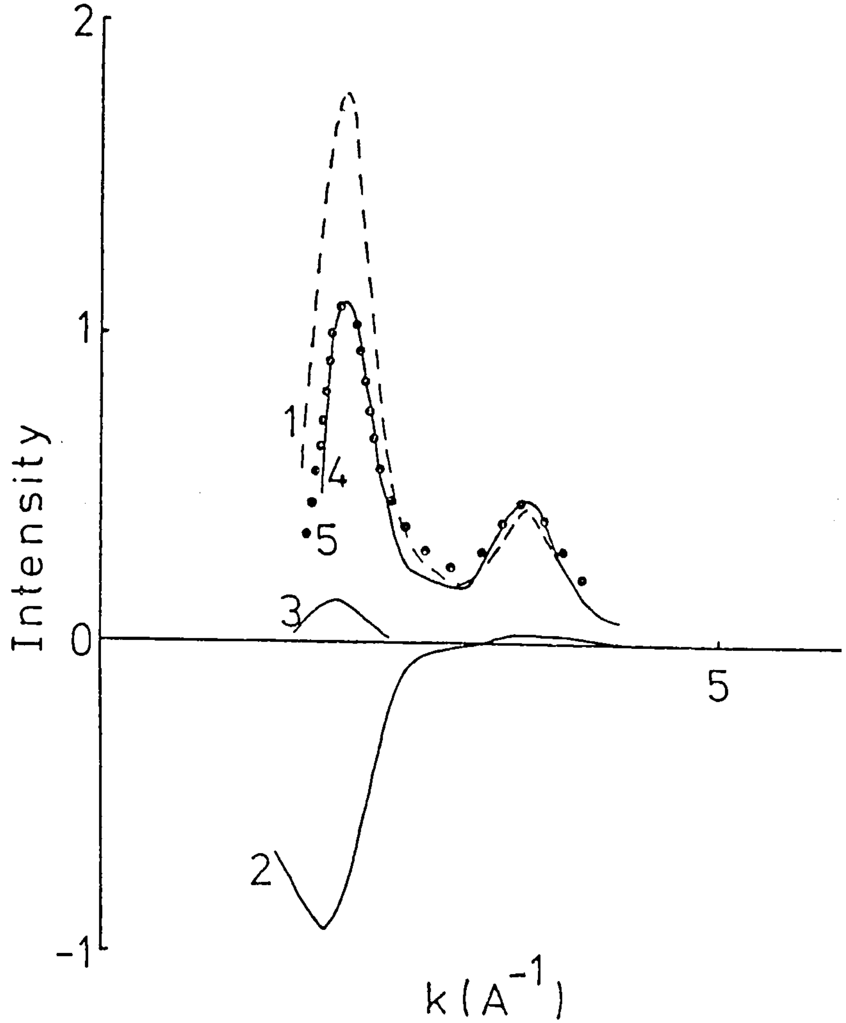

Figure 4.5 Electron scattering intensity for amorphous silicon using continuous random network model. Labelling (1) to (4) as in Figure 4.4. (5) Experiment[33].

distribution in Figure 4.1(c) accounts rather well for the 'forbidden' 222 reflection in crystalline Si. Naturally in the crystal, however, modern density functional theory combined with Bloch's theorem, leads to fully first principle electron densities, which can again be used to calculate Bragg reflection intensities[38].

Having emphasized that there is important information about chemical bonding in X-ray and electron diffraction intensities, let us return to liquid metals, and the important problem of electron–electron correlations among the valence electrons. Again, we shall find a (this time 'resonating') bond picture emerging, following earlier ideas of Pauling[39] on bonding in metals.

5 ELECTRON-ELECTRON PAIR CORRELATIONS IN LIQUID METALS

Returning to simple liquid metals like Na, these are really two-component liquids, Na^+ ions and valence electrons[40]. Thus, again, one wants to describe the structure in terms of three structure factors: the nuclear–nuclear structure factor $S(k)$, the valence electron–ion term $S_{iv}(\mathrm{k})$ and, of prime interest here, the electron–electron structure factor $S_{vv}(k)$[41].

Following Ref. 41, one writes the differential cross sections for X-ray and electron scattering in the forms

$$\left(\frac{d\sigma}{d\Omega}\right)_x = \text{const } S_x(k) \tag{5.1}$$

and

$$\left(\frac{d\sigma}{d\Omega}\right)_e = \frac{\text{const}}{k_4} S_e(k). \tag{5.2}$$

Then, $S_{vv}(k)$ can be written[41]

$$S_{vv}(k) = (1/Z)\{f_e(k)S_x(k) + f(k)S_e(k) - Zf(k)f_e(k)S(k)\} \tag{5.3}$$

Here $f(k)$ is the Fourier transform of the electron density in the core, while

$$f_e(k) = Z - f(k) \tag{5.4}$$

with Z the atomic number.

Thus, at least in principle, measurement via Eqs. (5.1) and (5.2) of $S_x(\mathrm{k})$ and $S_e(k)$, plus use of $S(k)$ determined by neutrons as already discussed in Section 2, will allow the electron–electron structure factor $S_{vv}(k)$ to be determined from Eq. (5.3), given a core scattering factor $f(k)$.

In practice, a number of difficulties remain[42,43,13]. However, by studying the main peaks of $S_x(k)$ and $S(k)$, it was originally argued in Ref. 41 that the X-rays were showing behaviour more like a 'Bragg peak' than the neutrons; the conclusion being that there was spatially more extensive short-range order of the electrons than the ions.

More recent work of Dobson[44] and of Johnson[45] has pressed the idea of Ref. 41 further for liquid Na and K respectively near their melting points. Both workers present evidence for short-range ordering over substantial differences and local coordination like that of a face-centered cubic (fcc) lattice. While in Ref. 41, Wigner electron correlations were referred to, these would lead to body-centered cubic (bcc) ordering.

Therefore, subsequent to the work of Dobson[44], March and Tosi[46] have presented an interpretation of the above fcc-like ordering in terms of a combination of both electron–electron and electron–ion interactions. They point out that a model which can explain the observed reflections characteristic of a fcc lattice in liquid Na and K can be built up by:

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a) Using sp^3 type bonding charges, with Pauling resonance invoked between occupied and unoccupied bonds and

b) Assuming, once local electron coordination characteristic of such bonds is formed, Wigner-type lattice ordering[47] can propagate the fcc lattice over distances of 30 to 40 Å.

In a little more detail, March and Tosi propose their model, after examining the X-ray diffraction pattern to be expected from a number of different models for the arrangement of bond charges. Models in which bond charges are placed between (a) all near-neighbour ions or (b) all next near-neighbour ions can be excluded. This is because, unless one breaks the correlations between first neighbour ions, one will necessarily obtain a diffraction pattern characteristic of a bcc structure, given that local ion ordering in the liquid just above the freezing point resembles that in the (bcc) crystal. Such a breaking of correlations has in fact been examined but still does not lead to an fcc diffraction pattern.

However, a model that does lead to fcc reflections is to consider bond charges between each ion and four of its near-neighbours, in a tetrahedral configuration. Again, in the language of chemical hybridization used in Section 4, we could think of mixing 3s and 3p atomic orbitals in Na say, with sp^3 hybridization once again. It is cautioned in Ref. 46 that atomic orbitals are poor as a starting point for Na, Wannier orbitals being more appropriate.

The tetrahedral configuration proposed[46] is shown in Figure 5.1. The electron 'bond charges' add up to a fcc lattice. The 'unoccupied' bonds to the remaining 4 corners of the cube from the body centre would have to resonate with those drawn in Figure 5.1, in the manner of Pauling[39].

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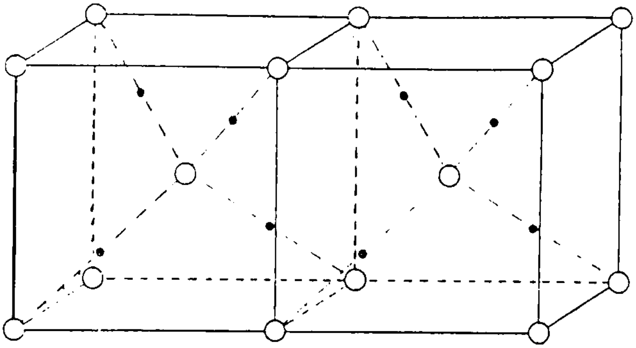

Figure 5.1 Electronic model proposed by March and Tosi[46] to interpret diffraction experiments from liquid Na near freezing. Bond charges (solid circles) are depicted schematically between each ion (open circles) and four of its near-neighbours, in tetrahedral array. 'Unoccupied' bonds to remaining 4 corners of cube would have to resonate[39] with those drawn in the Figure.

6 SUMMARY AND FUTURE DIRECTIONS

Having surveyed, by specific examples mainly, the information that can be derived from diffraction measurements on disordered systems, we wish to conclude by emphasizing areas that seem potentially fruitful for the future.

First of all, regarding the 'inverse problem' of Section 2.3, we have already stressed for a liquid metal like Na the interest in studying the variation of the force law with thermodynamic state along the coexistence curve. Of course, one has to recognise here that, eventually, as the critical point is approached, critical fluctuations 'take over' and numerous, though by no means all, properties become insensitive to the force law. More obviously, in the same area, accurate neutron diffraction data over a wide range of monentum transfer k should now allow effective pair interactions to be extracted from liquid state experiments for the technologically important transition metals.

Still on liquid metals, further understanding of supercooled liquids is clearly needed. A particularly relevant example in the present context is the work of Mountain[48] on supercooled liquid Rb. Though some diffraction experiments have been reported on liquid Ga[49], Mountain points out the difficulties to date in performing clean experiments of this type on simple supercooled liquids, and therefore the interest in computer simulation of this problem. By obtaining $g(r)$ for Rb, Mountain identifies two types of change as the temperature is lowered:

i) 'Sharpening' of the structure, which occurs in both equilibrium and supercooled liquid states:

ii) Evolution in the structure in the form of a shift in the position of the first maximum of $g(r)$ to larger r. This occurs in the equilibrium liquid but is not perceptible in the supercooled liquid[48].

Mountain notes in relation to the above that $g(r)$ represents the average environment of a particle. In the supercooled region, the near-neighbour environment becomes more sharply defined in space but does not shift its position as it does in the equilibrium liquid. That is to say, the local environment stops evolving, in the sense of a peak shift, once the freezing temperature is reached and in the supercooled region this fully developed liquid structure can only become more sharply defined until crystallization intervenes. Also in Ref. 48, following earlier studies[50,51], Mountain reiterates (cf. Section 2.2 above) that another empirical freezing criterion comes back in terms of the ratio R of the magnitude of $g(r)$ at the first minimum to the magnitude at the first maximum as $R = 0.20 \pm 0.01$. Further, R is linear with temperature for liquid states. Clearly, this work prompts further studies, both scattering experiments and approximate liquid state theory, on both the liquid-crystal phase transition and on the less well explored area of supercooling.

Related to this, there has been a resurgence of interest in the glassy transition. The work of Bernu *et al.*[52], again by computer experiment, is notable; however, so far the generalization to the dynamic structure factor has been the most fruitful approach here and it would take us too far from our main theme to give more than a few central references here[53,54].

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Finally, let us return to chemical bonding in disordered systems. While in materials like amorphous silicon and carbon, the existence of well defined covalent bonds has been recognised for decades, it is, of course, extremely interesting that evidence for chemical bonding in low electron density metals like the alkalis is building up strongly (see Section 5 for liquid Na: and Refs. 55 and 56 for the crystalline phase of this sp metal).

Some stimulation for investigating sp metals further in the solid state has come from a desire to find a theory of superconductivity which would embrace both the recently discovered high T_c ceramic oxides[57] and the simple metals. As an example, the work of Messmer[58] on crystalline Be metal can be sited; here, as for the liquid alkalis discussed in Section 5, both chemical- and Wigner-lattice-type arguments are invoked for strong spatial correlations between valence electrons; the present writer[59] has drawn attention recently to the possible link between Dobson's analysis[42] of diffraction data on the trivalent liquid metal Al and Messmer's ideas[58] on divalent crystalline hexagonal-close-packed Be. There seems no doubt that there is currently a great deal more to be done in exploiting fully, by a combination of diffraction experiments and first-principles theory, just what we can learn as to the combined role of electron-ion and electron-electron interactions in both ionic structural correlations and pair correlations between valence electrons. Chemical insight is surely going to be of great importance in these future studies, even in metals like Na and Al which were thought, for a very long time, to be almost 'ideal' examples of electron delocalization.

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