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The density of states of a model of a topologically disordered solid

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Abstract. The results of a previous paper by the authors, which express the density of states for the Thorpe–Weaire model in terms of the number of returns to the origin, are generalized to the case of arbitrary coordination numbers, and the condition for the existence of a band gap obtained by studying the convergence of the series for the resolvent. The asymptotic form of the series is used to obtain the form of the density of states near the band edges for a topologically disordered lattice. It is found to be exactly the same as that for the periodic case.

1. Introduction

Weaire and Thorpe (1971) have introduced a hamiltonian which can form a starting point for the study of disordered materials of the amorphous type. In a previous paper (Lukes and Nix 1973, to be referred to as I) we have obtained an expression for the density of states for this model in terms of the number of returns to the origin. Explicit results for the density of states were, however, only obtained for the case of a periodic lattice. In the present paper we pursue our method further for the case of a disordered material. To do so we argue that the assumptions made in the model limit rather specifically the type of disorder which can obtain. We are thus able to use existing results on the number of returns to the origin to calculate the form of the density of states near the band edges. The condition for the existence of energy gaps for general coordination number W is also found. Our results for the density of states suggest that the model does not depart sufficiently from the electronic structure of the periodic lattice and requires further modification if the properties of the amorphous material are to be adequately represented.

2. The expression for the density of states for general coordination number

As a starting point we outline the method used in I, where we consider the two-band hamiltonian of Weaire and Thorpe (1971):

$$\boldsymbol{H} = V_1 \sum_{\substack{i \\ j \neq j'}}{}' |ij\rangle\langle ij'| + V_2 \sum_{\substack{i \neq i' \\ j}} |ij\rangle\langle i'j|\delta_{i,S_j^i} \equiv \boldsymbol{H}_1 + \boldsymbol{H}_2 \tag{2.1}$$

where $|ij\rangle$ refers to the valence orbital associated with site i whose bond index is j, the

symbol δ_{i,S_i^j} being defined as

$$\delta_{i,S_i^j} \begin{cases} = 1 \text{ if } i' \text{ is the nearest neighbour of atom } i \text{ associated with bond } j \\ = 0 \text{ otherwise.} \end{cases}$$

With this separation of $\boldsymbol{H}$ into $\boldsymbol{H}_1$ and $\boldsymbol{H}_2$ we then defined a zero-order resolvent $\boldsymbol{G}_0$ as

$$\boldsymbol{G}_0 = (E\boldsymbol{I} - \boldsymbol{H}_1)^{-1} \tag{2.2}$$

whose matrix elements were given by

$$\langle ij|\boldsymbol{G}_0|kl\rangle = \delta_{i,k}(A + B\delta_{j,l})$$

where

$$A = \frac{V_1}{(E-3V_1)(E+V_1)}, \qquad B = \frac{1}{E+V_1}. \tag{2.3}$$

The averaged density of states per particle was defined in the usual way in terms of $\boldsymbol{G}^+ = (E - \boldsymbol{H} + \mathrm{i}\epsilon)^{-1}$ as

$$n(E) = -(\pi N)^{-1} \operatorname{Im} \sum_{i,j} \langle ij|\boldsymbol{G}^+|ij\rangle \tag{2.4}$$

Dyson's equation was then used to find

$$\langle ij|\boldsymbol{G}^+|ij\rangle = \sum_{n=0}^{\infty} \langle ij|\boldsymbol{T}_n|ij\rangle$$

where $\boldsymbol{T}_n = \boldsymbol{G}_0\boldsymbol{H}_2\boldsymbol{G}_0 \ldots \boldsymbol{H}_2\boldsymbol{G}_0$ contains N factors of $\boldsymbol{H}_2$. It was precisely these N factors of $\boldsymbol{H}_2$ which made $\langle ij|\boldsymbol{T}_n|ij\rangle$ dependent upon the number of returning walks of length t to atom i, denoted by $N(t, i, i)$. We then proceeded via a rather lengthy piece of algebra to obtain the following two recurrence relationships for the matrix elements of $\boldsymbol{T}_n$:

$$\sum_{ij} \langle ij|\boldsymbol{T}_n|ij\rangle = \frac{2A(2A+B)}{(4A+B)^2} \sum_{i,j,l} \langle ij|\boldsymbol{T}_n|il\rangle + V_2^2B^2 \sum_{i,j} \langle ij|\boldsymbol{T}_{n-2}|ij\rangle \tag{2.5}$$

$$\sum_{i,j,l} \langle ij|\boldsymbol{T}_n|il\rangle = V_2^n(4A+B)^2 \left(\frac{A}{V_2^{n-1}(4A+B)^2} \sum_{i,j,l} \langle ij|\boldsymbol{T}_{n-1}(N(t+1, i, i))|il\rangle \right.$$
$$\left. + \frac{B(4A+B)}{V_2^{n-2}(4A+B)^2} \sum_{i,j,l} \langle ij|\boldsymbol{T}_{n-2}(N(t, i, i))|il\rangle \right). \tag{2.6}$$

Using the above relationships we were able, by collecting coefficients of $N(t, i, i)$ to obtain the following:

$$\sum_{i,j} \langle ij|\boldsymbol{G}^+|ij\rangle = \sum_i \left[\frac{2BN(0, i, i)}{1-V_2^2B^2} + \frac{V_2B^2N(1, i, i)}{1-V_2^2B^2} + \frac{2(2A+B)}{1-z} \sum_{t=0}^{\infty} \left(\frac{V_2A}{1-z} \right)^t N(t, i, i) \right] \tag{2.7}$$

where $z = V_2^2B(4A+B)$. Finally we were able, by the use of (2.4), to write down the density of states as

$$n(E) = -\frac{1}{\pi N} \operatorname{Im} \sum_i \left[\frac{2BN(0, i, i)}{1-V_2^2B^2} + \frac{V_2B^2N(1, i, i)}{1-V_2^2B^2} + \frac{2(2A+B)}{1-z} \sum_{t=0}^{\infty} \left(\frac{V_2A}{1-z} \right)^t N(t, i, i) \right]. \tag{2.8}$$

We now generalize the above results to the case of general coordination number W.

The matrix representing $\boldsymbol{G}_0$ is still of block diagonal form, but instead of 4×4 matrix entries we have $W \times W$ matrix entries, which lead to the following definitions for A and B

which occur in (2.3), ie:

$$A = \frac{V_1}{[E-(W-1)V_1](E+V_1)}, \qquad B = \frac{1}{E+V_1}.$$

In the working that followed only the following alterations need be made:

$$(4A+B) \mapsto (WA+B)$$
$$2A(2A+B) \mapsto A(WA+2B)$$

for example, equations (2.5), (2.6) and (2.7) become

$$\sum_{i,j} \langle ij|\boldsymbol{T}_n|ij\rangle = \frac{A(WA+2B)}{(WA+B)^2} \sum_{i,j,l} \langle ij|\boldsymbol{T}_n|il\rangle + V_2^2 B^2 \sum_{i,j} \langle ij|\boldsymbol{T}_{n-2}|ij\rangle \tag{2.9}$$

$$\sum_{i,j,l} \langle ij|\boldsymbol{T}_n|il\rangle = V_2^n (WA+B)^2 \left(\frac{A}{V_2^{n-1}(WA+B)^2} \sum_{i,j,l} \langle ij|\boldsymbol{T}_{n-1}(N(t+1,i,i))|il\rangle \right.$$
$$\left. + \frac{B(WA+B)}{V_2^{n-2}(WA+B)^2} \sum_{i,j,l} \langle ij|\boldsymbol{T}_{n-2}(N(t,i,i))|il\rangle \right) \tag{2.10}$$

$$\sum_{i,j} \langle ij|\boldsymbol{G}|ij\rangle = \sum_i \left[\frac{2BN(0,i,i)}{1-V_2^2B^2} + \frac{V_2B^2N(1,i,i)}{1-V_2^2B^2} + \frac{WA+2B}{1-z} \sum_{t=0}^{\infty} \left(\frac{V_2A}{1-z} \right)^t N(t,i,i) \right], \tag{2.11}$$

where $z = V_2^2B(WA+B)$. Thus finally we have the following expression for the average density of states of a W-fold coordinated structure:

$$n(E) = -\frac{1}{\pi N} \operatorname{Im} \sum_i \left[\frac{2BN(0,i,i)}{1-V_2^2B^2} + \frac{V_2B^2N(1,i,i)}{1-V_2^2B^2} + \frac{WA+2B}{1-z} \sum_{t=0}^{\infty} \left(\frac{V_2A}{1-z} \right)^t N(t,i,i) \right] \tag{2.12}$$

where $z = V_2^2B(WA+B)$.

3. The condition for the existence of an energy gap

The quantity $N(t,i,i)$ is the number of returns to the origin i after t steps and, in I, this was only evaluated for a periodic lattice. To calculate it for present problem we note that the hamiltonian of Weaire and Thorpe (1971) assumes constant overlap integrals V_1 and V_2.

Figure 1 illustrates the structure of a typical fourfold coordinated lattice. Since the overlap integrals are assumed constant this implies constant bond lengths and the bond angle between $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$ is also constant. Thus the most general form of disorder is obtained by rotating the lower tetrahedron about the $\boldsymbol{r}_1$ axis along the dashed contour. We make the assumption that all angles in such a rotation are equally likely, which is the maximum disorder allowed by the model. This presumably overestimates the disorder since there are in a real amorphous lattice, connectivity requirements on neighbouring atoms which are probably more stringent. On the other hand, even with this maximum degree of disorder, we shall later see that with the assumption of constant overlap integrals the results for the density of states near the band edges agree with those of the periodic lattice.

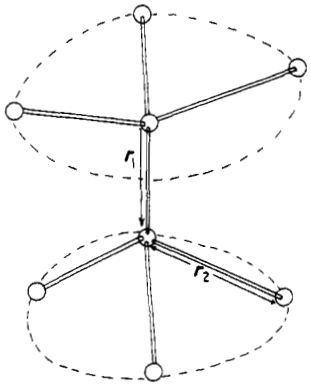

Figure 1. The structure of a typical fourfold coordinated topologically disordered lattice. The bond angle between r_1 and r_2 is assumed to be constant and the tetrahedra can be rotated anywhere along the dashed contour.

To calculate $N(t, 0, 0)$ we use the fact that $N(t, 0, 0)/W^t$ is the probability of the walk returning to the origin. For a random walk on a lattice this is asymptotically proportional to $t^{-3/2}$. For the more general case considered here Tchen (1952) has shown that for large t the probability of returning to the origin is still proportional to $t^{-3/2}$.

Finally, we may say that the asymptotic (ie large t) convergence properties of the resolvent in the presence of topological disorder are determined by the convergence properties of the following series:

$$\sum_{t=0}^{\infty} \left(\frac{V_2 A}{1-z}\right)^t N(t, 0, 0),$$

where for large t

$$\frac{N(t, 0, 0)}{W^t} \propto t^{-3/2}$$

ie

$$\frac{N(t, 0, 0)}{W^t} = \text{constant} \times t^{-3/2}.$$

Thus

$$\sum_{t=0}^{\infty} \left(\frac{V_2 A}{1-z}\right)^t N(t, 0, 0) \sim \text{constant} \times \sum_{t=0}^{\infty} \left(\frac{W V_2 A}{1-z}\right)^t t^{-3/2}.$$

We now use the fact that convergence of the resolvent series in a given region of energy implies that this operator is bounded and hence that there are no eigenvalues in that region. Such an approach to the existence of energy gaps has also been used by Schwartz and Ehrenreich (1972).

By applying the ratio test we then obtain the following inequality for the energy bands, namely:

$$\lim_{t\to\infty} \left| \frac{c^t t^{-3/2}}{c^{t+1}(t+1)^{-3/2}} \right| < 1, \qquad c = \frac{W V_2 A}{1-z}.$$

This leads to the condition

$$0 > [(E+V_1)^2-(E+V_1)WV_1-V_2^2-W|V_1V_2|][(E+V_1)^2-(E+V_1)WV_1-V_2^2+W|V_1V_2|].$$

The roots of the first factor are

$$E = V_2+(W-1)V_1 \qquad \text{or} \qquad -V_1-V_2$$

and similarly for the second factor

$$E = -V_2+(W-1)V_1 \qquad \text{or} \qquad -V_1+V_2.$$

By investigating the sign of the above two quadratics in the regions defined by the four roots given, the only ranges of E to satisfy the above inequalities are

$$(W-1)V_1+V_2 \leqslant E \leqslant -V_1+V_2$$
$$(W-1)V_1-V_2 \leqslant E \leqslant -V_1-V_2$$

(which give the limits of the two bands), that is,

$$\frac{(W-1)V_1}{|V_2|}-1 \leqslant \frac{E}{|V_2|} \leqslant -1-\frac{V_1}{|V_2|}$$
$$1+\frac{(W-1)V_1}{|V_2|} \leqslant \frac{E}{|V_2|} \leqslant 1-\frac{V_1}{|V_2|}$$

since V_1 and $V_2 < 0$ in this model.

If $W = 4$ the ranges become

$$-\frac{3|V_1|}{|V_2|}-1 \leqslant \frac{E}{|V_2|} \leqslant -1+\frac{|V_1|}{|V_2|}$$
$$1-\frac{3|V_1|}{|V_2|} \leqslant \frac{E}{|V_2|} \leqslant 1+\frac{|V_1|}{|V_2|}$$

which agrees with a result obtained by Schwartz and Ehrenreich (1972) by a different method.

It is interesting to note in passing, that the regions are distinct (ie an energy gap exists) only if

$$(W-1)V_1-V_2 > -V_1+V_2,$$

that is,

$$\frac{|V_1|}{|V_2|} < \frac{2}{W}.$$

4. The form of the density of states near the band edges

In this section we investigate the form of $n(E)$ near the band edges where $WV_2A/(1-z) \sim 1$. To do this we look at the behaviour of the following series:

$$\sum_{t=0}^{\infty} \frac{c^t}{t^{3/2}} \qquad \text{as } c \sim 1^-.$$

Now $c^t = e^{t \ln c}$ but $1-c \sim 0^+$. Hence $\ln c = \ln[1-(1-c)] \sim -(1-c)$. The series therefore behaves like

$$\sum_{t=0}^{\infty} \frac{e^{-(1-c)t}}{t^{3/2}}$$

which in turn behaves like

$$\int_0^{\infty} \frac{e^{-(1-c)t}}{t^{3/2}} dt = (1-c)^{1/2}\Gamma(-\tfrac{1}{2}).$$

With this result we can now analytically continue this series locally into the region $c \sim 1^+$.

The above procedure has been rigorously justified by Domb *et al* (1959). They proved that it was the large order moments of $n(E)$ (which in site representation means large number of walks), that determine the behaviour of $n(E)$ near the upper band edge.

Applying these results to the series for $n(E)$ we obtain that

$$\sum_{t=0}^{\infty} \left(\frac{V_2 A}{1-z}\right)^t N(t,0,0) \sim \alpha\Gamma(-\tfrac{1}{2})\left(1-\frac{WV_2A}{1-z}\right)^{1/2},$$

where α is the constant of proportionality between $N(t,0,0)/W^t$ and $t^{-3/2}$ implied in Tchen's work. It is shown in appendix 1 that this constant is identical with that for the periodic lattice.

The above is true for energies in the immediate locality of the points defined by

$$\frac{WV_2A}{1-z} = 1$$

ie when $E = -V_1 - V_2$ or $V_2 + V_1(W-1)$ which correspond to the uppermost and lowermost limits of the energy bands. The case $c = -1$ would similarly give the behaviour near the remaining two interior band edges, but the properties of the series near there are more complicated. Hence

$$n(E) = -\frac{1}{\pi} \operatorname{Im} \frac{WA+2B}{1-z} \alpha\Gamma(-\tfrac{1}{2})\left(1-\frac{WV_2A}{1-z}\right)^{1/2}$$

in the regions defined above. Now

$$z = \frac{V_2^2}{[2E-(W-1)V_1](E+V_1)}$$

and

$$WA+2B = \frac{2E+2V_1-WV_1}{[E-(W-1)V_1](E+V_1)}.$$

Therefore

$$n(E) \sim -\frac{1}{\pi} \operatorname{Im} \frac{(2E+2V_1-WV_1)\alpha\Gamma(-\frac{1}{2})}{\{[E-(W-1)V_1](E+V_1)-V_2^2\}^{3/2}} \{[E-(W-1)V_1](E+V_1)-V_2^2 - WV_1V_2\}^{1/2} \tag{4.1}$$

when $E \sim -V_1 - V_2$ or $E \sim V_2 + (W-1)V_1$.

4.1. $E \sim -V_1 - V_2$

In this case

$$n(E) \sim -\frac{\alpha}{\pi}\Gamma(-\tfrac{1}{2})\,\mathrm{Im}\lim_{\epsilon\to 0}\frac{(-WV_1-2V_2+i\epsilon)(-WV_1-2V_2+i\epsilon)^{1/2}(E+V_1+V_2+i\epsilon)^{1/2}}{[(-V_2+i\epsilon)(-V_2-WV_1+i\epsilon)-V_2^2]^{3/2}}$$

but $E+V_1+V_2 < 0$ when E is in the band. Hence

$$n(E) \sim \frac{2\alpha}{\pi^{1/2}}\frac{(-WV_1-2V_2)^{3/2}}{(WV_1V_2)^{3/2}}(-V_1-V_2-E)^{1/2}. \tag{4.2}$$

4.2. $E \sim V_2+(W-1)V_1$

Here $E+V_1+V_2 \sim 2V_2+WV_1 < 0$ and

$$n(E) \sim \frac{2\alpha}{\pi^{1/2}}\frac{(-2V_2-WV_1)^{3/2}}{(WV_1V_2)^{3/2}}\{E-[V_2+(W-1)V_1]\}^{1/2}. \tag{4.3}$$

The form of the density of states near the band edges is thus identical with that for the periodic lattice. This result has also been obtained by Ziman (1971). Since experimental results which reflect the density of states, such as optical absorption, strongly suggest that the density of states of the amorphous material differs more radically from that in the periodic case, it appears then, that the model here adopted would need to be modified to represent adequately the properties of the disordered system. The removal of the assumption that the overlap integrals are constants would form perhaps the most obvious first step.

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Appendix 1. To identify the constant of proportionality for $N(t, 0, 0)$

If we let $\boldsymbol{R}$ denote the end-to-end position vector of N walks $\boldsymbol{r}_i (i = 1, \ldots, N)$, ie

$$\boldsymbol{R} = \sum_{i=1}^{N} \boldsymbol{r}_i, \tag{A1.1}$$

then Tchen (1952) and Chandrasekhar (1943) respectively, have shown for the case of a freely-rotating chain, and for any lattice, that $\boldsymbol{R}$ is normally distributed with normalization constant

$$(\tfrac{2}{3}\pi\langle \boldsymbol{R}^2\rangle)^{-3/2} \tag{A1.2}$$

where the angular bracket denotes an average over all possible configurations of the chain obtained by rotations about each bond axis. With this result, we now have to show that the values both of $\langle \boldsymbol{R}\rangle$ and $\langle \boldsymbol{R}^2\rangle$ must be the same in each case, for the probability of returning to the origin to be the same. Chandrasekhar finds quite generally that for any lattice $\langle \boldsymbol{R}\rangle = 0$ and $\langle \boldsymbol{R}^2\rangle = nl^2$, where l is the nearest neighbour distance.

For a freely-rotating chain we proceed as follows: figure 2 shows all possible positions P_1, P_2, P_3, and P_4 of some $\boldsymbol{r}_i$ in a given configuration, and it can be seen, either by symmetry, since P_1, P_2, P_3, P_4 are the vertices of a regular tetrahedron, or by direct calculation, that the average of $\boldsymbol{r}_i$ for each configuration is **0**. Therefore we have

$$\langle \boldsymbol{R} \rangle = \sum_{i=1}^{N} \langle \boldsymbol{r}_i \rangle = \boldsymbol{0}$$

and

$$\langle \boldsymbol{R}^2 \rangle = \left\langle \left(\sum_{i=1}^{N} \boldsymbol{r}_i \right) \cdot \left(\sum_{j=1}^{N} \boldsymbol{r}_j \right) \right\rangle = \sum_{i=1}^{N} \langle \boldsymbol{r}_i^2 \rangle + 2 \sum_{i<j} \langle \boldsymbol{r}_i \cdot \boldsymbol{r}_j \rangle \tag{A1.3}$$

where, since each bond length is constant,

$$\sum_{i=1}^{N} \langle \boldsymbol{r}_i^2 \rangle = nl^2.$$

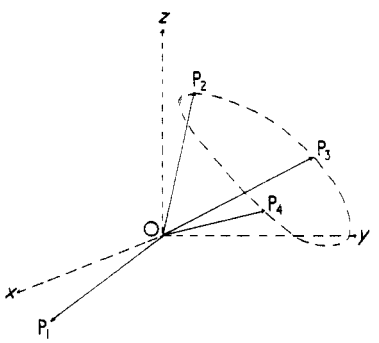

Figure 2. For each walk in the chain there are four possible directions, $\overrightarrow{OP_1}$, $\overrightarrow{OP_2}$, $\overrightarrow{OP_3}$ and $\overrightarrow{OP_4}$. Each configuration corresponds to different positions on the dashed contour.

To calculate the second term of (A1.3) we use the method adopted by Flory (1969) who used the following argument. To find $\langle \boldsymbol{r}_i \cdot \boldsymbol{r}_j \rangle$ for any particular i and j is equivalent to finding the averaged projection of $\boldsymbol{r}_j$ onto $\boldsymbol{r}_{j-1}$ (since the averaged projection perpendicular to this vector is zero by symmetry), then of this projection onto $\boldsymbol{r}_{j-2}$, and so on down to $\boldsymbol{r}_i$. However, in our problem $\langle \boldsymbol{r}_{j-1} \cdot \boldsymbol{r}_j \rangle$ is an average along one of the directions $\overrightarrow{P_iO}$ shown in figure 2, and hence by symmetry is zero. Thus $\langle \boldsymbol{r}_i \cdot \boldsymbol{r}_j \rangle = 0$ for all $i \neq j$, and (A1.3) becomes

$$\langle \boldsymbol{R}^2 \rangle = nl^2$$

which is the same as that for the lattice. Therefore the probability of a returning walk is given in both cases by $(\frac{2}{3}\pi l^2 n)^{-3/2}$.

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