A note on quasielastic neutron scattering
G. Coddens

To cite this version:

HAL Id: jpa-00246955
https://hal.archives-ouvertes.fr/jpa-00246955
Submitted on 1 Jan 1994

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers. L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
A note on quasielastic neutron scattering

G. Coddens

Laboratoire Léon Brillouin, C.E.A./C.N.R.S., F-91191 Gif-sur-Yvette Cedex, France
Neutron Scattering Project, I.I.K.W., University of Antwerp, B-2610-Wilrijk, Belgium

(Received 7 October 1993, revised 11 February 1994, accepted 24 February 1994)

Abstract. — We present a theorem that in coherent quasielastic neutron scattering on a confined and limited system of identical particles only the configuration-configuration correlations have to be examined without any hindsight on the distribution of the particles inside the configuration. This constitutes a strong simplification with respect to the problem where all particle-particle correlations would have to be accounted for. The method is illustrated on an example of correlated hopping on a piece of an octagonal quasiperiodic tiling. With some modifications the method can also be used for incoherent scattering. A further simplification of the calculations both for coherent and incoherent scattering functions is obtained by introducing a new matrix notation that allows fully for the symmetry properties of the problem.

1. Introduction.

Quasielastic neutron scattering is a powerful technique to study diffusive motions in condensed matter [1, 2]. In general the experimental data are analysed by comparing them with the scattering functions $S_{\text{inc}}(Q, \omega)$ and $S(Q, \omega)$ calculated from a model. In a large number of situations one can use so-called jump models. Although this approach definitely contains approximations [3, 4], in practise it very often works rather well. Correct quantum mechanical calculations are difficult [4]. A large amount of such jump model calculations have been carried out for the incoherent scattering function $S_{\text{inc}}(Q, \omega)$; for bounded motion the concept of the EISF (elastic incoherent structure factor) was introduced [5], and developed in depth for many physical applications [6]. For coherent scattering, calculations of $S(Q, \omega)$ are however scarce, as it turns out to be difficult to take into account the correlations between the different particles. In the present note we propose a method that may be instrumental in tackling this problem.

2. A theorem for coherent scattering.

According to Van Hove [7] the incoherent and total scattering functions are given by:

$$S_{\text{inc}}(Q, \omega) = \frac{k_f}{k_i} \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} e^{-i\omega t} \sum_j b_j^2 \langle e^{iQ(r_j(t) - r_j(0))} \rangle_{\text{th}} \, dt$$

(1)
\[ S(Q, \omega) = \frac{k_f}{k_i} \frac{1}{2\pi \hbar} \int_{-\infty}^{\infty} e^{-i\omega t} \sum_{j,k} b^*_j b_k \langle e^{iQ \cdot (r_k(t) - r_j(0))} \rangle_{th} dt \]  

(2)

Here, \( k_i, k_f \) are the wave vectors of the incoming and outgoing neutron, \( \hbar Q \) and \( \hbar \omega \) are the neutron momentum and energy transfers, \( b_j \) and \( b_k \) are the scattering lengths and \( r_k(t) \) is the position of particle \( k \) at time \( t \); \( \langle \cdot \rangle_{th} \) stands for thermal average. Whereas the incoherent scattering function involves only correlations between a particle and itself, the total scattering function contains also correlations between different particles. Incoherent and coherent neutron scattering provide a beautiful illustration of the particle-wave duality in quantum mechanics.

Coherent scattering corresponds to the neutron acting as a wave, while incoherent scattering describes the particle behaviour of the neutron. This has been expounded in a superb way by Feynman [8]: it becomes possible to reconstruct the path of the neutron in the scattering process if its interaction with the scattering nucleus tags this nucleus by changing its state. E.g. if the spin of a spin 1/2 nucleus is flipped we know afterwards that it is this particular nucleus that has scattered the neutron. Hence the neutron has behaved as a particle with a well defined path and the scattering process is incoherent. If, on the contrary, there is no way to tell which path the neutron has taken, since no nucleus has been tagged, then the neutron has behaved as a wave and been scattered coherently. The fact that no atoms have been tagged means that they stay indistinguishable in the following sense: if a configuration or cluster of \( n \) identical atoms \( C_1(0) \) at time 0 evolves to a configuration \( C_2(t) \) at time \( t \), then no information will be available about the atoms in \( C_2(t) \) apart from the configuration; there can be no information about possible permutations between the atoms within \( C_2 \) since this would imply the presence of a kind of tagging allowing us to find out about these permutations. From this argument we conclude that the appropriate language to speak about coherent scattering should not be in terms of particle correlations but rather in terms of configuration correlations. This can be proved rigorously if we assume all particles to be identical. Let us introduce the notation:

\[ \langle v_1, v_2, \ldots, v_n \rangle \otimes_Q \langle u_1, u_2, \ldots, u_n \rangle = \sum_{j=1}^{n} e^{iQ \cdot v_j} e^{-iQ \cdot u_j} \]

(3)

Here \( (v_j)_{j=1}^{n} \) and \( (u_j)_{j=1}^{n} \) typically describe a configuration of \( n \) particles with position vectors \( v_j \) or \( u_j \). Let \( G(n) \) be the group of \( n! \) permutations of \( (1, 2, \ldots, j, \ldots, n) \). We further define the cyclic permutations \( \mathcal{P}_k : (1, 2, \ldots, n) \rightarrow (1 \oplus k, 2 \oplus k, \ldots, n \oplus k) \), where the signs \( \oplus \) indicate sums to be taken modulo \( n \). We also write \( \mathcal{P}(r_1, r_2, \ldots, r_n) = (r_{\mathcal{P}(1)}, \ldots, r_{\mathcal{P}(n)}) \), \( \forall \mathcal{P} \in G(n) \). Now by definition, the intermediate scattering function \( I(Q, t) \) is given by:

\[
\frac{2\pi \hbar}{b^2} \frac{k_i}{k_f} I(Q, t) = \sum_{j=1}^{n} \sum_{k=1}^{n} \langle e^{iQ \cdot r_j(t)} e^{-iQ \cdot r_k(0)} \rangle_{th} = \\
= \langle \sum_{j=1}^{n} (\mathcal{P}_{j-1}(r_1(t), r_2(t), \ldots, r_n(t))) \rangle \otimes_Q \langle r_1(0), r_2(0), \ldots, r_n(0) \rangle_{th}
\]

(4)

In fact, suppose that we write the terms \( \exp(iQ \cdot (r_j(t) - r_k(0))) \) in a matrix at positions \((k,j)\). The first line of equation (4) says then that we have to make the sum over all the elements of this matrix. In the second line the same sum is obtained by first adding the \( n \) terms on the diagonal, i.e. the elements \((1, 1), (2, 2), \ldots (n, n)\). This is the contribution from the terms containing \( \mathcal{P}_0 \). The terms containing \( \mathcal{P}_1 \) correspond to the elements on the parallel diagonal \((1, 2), (2, 3), \ldots (n-1, n), (n, 1)\), i.e. to the elements \( (k, \mathcal{P}_1(k)) \). This way the \( n^2 \) combinations \((k, j)\) are counted by introducing the \( n \) cyclic permutations and the symbol \( \otimes_Q \).
which also contains \( n \) terms. We abbreviate further \( C^T = (r_1, r_2, \ldots, r_n) \) and \( f = 2\pi \hbar k_1/k_1 b^2 \). We can put \( C(t) = P^\circ T(t)C(0) \) with some \( P \in \mathcal{G}(n) \); here \( T(t) \) can be a matrix but could also be a more general matrix function, and it describes the configurational changes, while \( P \) describes a possible permutation of the particles that has taken place inside the cluster.

In this way

\[
f I(Q, t) = \left( \sum_{k=1}^{n} (P_{k-1} C(t)) \square Q C(0) \right)_{th} = \frac{1}{(n-1)!} \left( \sum_{\pi \in \mathcal{G}(n)} (\pi C(t)) \square Q C(0) \right)_{th} = \frac{1}{(n-1)!} \left( \sum_{\pi \in \mathcal{G}(n)} (\pi \circ P \circ T(t)C(0)) \square Q C(0) \right)_{th} = \frac{1}{(n-1)!} \left( \sum_{\pi \in \mathcal{G}(n)} (\pi \circ T(t)C(0)) \square Q C(0) \right)_{th} = \left( \sum_{k=1}^{n} (P_{k-1} \circ T(t)C(0)) \square Q C(0) \right)_{th}
\]

(5)

The idea behind the preceding lines is as follows. Suppose we write again the elements \( \exp(iQ \cdot (r_j(t) - r_k(0))) \) in a matrix. However, this time on the diagonal we write the elements \( (j, \Pi(j)) \), with \( \Pi \in \mathcal{G}(n) \), and on the parallel diagonals we write \( (j, \mathcal{P}_k \Pi(j)) \). The sum of all the elements of the matrix will still be the same. The relation \( \Pi_1 \equiv \Pi_2 \iff (\exists k \in [0, n-1] \cap \mathbb{N})(\mathcal{P}_k \Pi_1 = \Pi_2) \) is an equivalence relation. The corresponding quotient structure defines a partition of \( \mathcal{G}(n) \) in \( (n-1)! \) classes \( \mathcal{C}(\Pi) \). We can thus rewrite the sum \( \sum_{j=1}^{n} \sum_{k=1}^{n} \text{term}(j, \mathcal{P}_k \Pi(j)) \) as \( \sum_{j=1}^{n} \sum_{\Pi_k \in \mathcal{C}(\Pi)} \text{term}(j, \Pi_k(j)) \). Each of these classes corresponds to a matrix yielding an identical value for the sum. This explains why we can replace these sums by \( \frac{1}{(n-1)!} \sum_{j=1}^{n} \sum_{\pi \in \mathcal{G}(n)} \text{term}(j, \pi(j)) \). The final result expresses that we can calculate the coherent scattering function by using the time evolution of the configurations, since any trace of \( \mathcal{P} \) has been lost in the final line of equation (5), due to the group properties of \( \mathcal{G}(n) \) (which intervene when we replace the sum over \( \pi \circ \mathcal{P} \) by the sum over \( \pi \)). Note that in the preceding lines \( \mathcal{P} \) corresponds to a physical reality while the \( \mathcal{P}_{k-1} \) are just mathematical expedients introduced to count the combinations \((k, j)\).

When a particle jumps between two neighbouring sites with a characteristic time \( \tau \), in the language of clusters one can say that the system jumps between two ("neighbouring") configurations with the same characteristic time. This can even be generalised to cases where several particles jump in a correlated way, provided that each move still corresponds to a change of configuration. Each jump of a particle (or set of particles) corresponds then to a jump of the system. The system can thus be considered as an abstract particle and the different configurations as abstract sites. In the case when the number of configurations is limited this abstract isomorphism will make it possible to write the rate equations linking various clusters in the same matrix form as for the jumps of a single particle between different sites:

\[
\frac{dP}{dt} + S^{-1} \Lambda(t)SP = 0
\]

(6)

The so-called jump matrix \( M = S^{-1} \Lambda(t)S \), where \( \Lambda \) is diagonal or more generally of the Jordan form, represents the cluster-cluster transition probabilities; often \( \Lambda \) will be independent of \( t \).
The solution of the matrix equation (6) is given by:

\[ SP(t) = \exp(-\int_0^t \Lambda(u) du) SP(0) \]  

(7)

In equations (6) and (7) \( P \) is a \( 1 \times m \) matrix and \( P_j(t) \) gives the probability to find the system in configuration \( C_j \) at time \( t \); \( m \) is the number of different (indistinguishable) configurations. In the more conventional methods to calculate the incoherent scattering function as described in reference [2] a set of linear equations analogous to (6) is obtained; however, in those cases the elements \( P_i \) of the column matrix \( P \) give the probabilities to find a particle at site \( i \) at time \( t \). The meaning of these quantities is thus quite different, despite the formal analogy (which is the result of the abstract isomorphism); they do not refer to particles in the present case. The formalism can only be carried out easily if each jump of a particle (or each set of simultaneous jumps of particles) corresponds to a change of configuration. In the calculation of the thermal average one has to consider different problems of the type (6), depending on the system being in the configuration \( C_1, C_2, ..., C_m \) at the moment \( t = 0 \). We will further note these \( m \) different matrices as \( P^{(1)}, P^{(2)}, ..., P^{(m)} \). It is clear that

\[ P^{(1)}(t) = S^{-1} \exp(-\int_0^t \Lambda(u) du) S(p_1, 0, 0, 0, ..., 0)^T \]  

(8)

where \( p_1 \) is the probability that the system is in configuration \( C_1 \) at \( t = 0 \). \( P^{(i)}(t) = p_1(t) \), is the probability that the system is in configuration \( C_j \) at time \( t \), if it was in configuration \( C_i \) at time \( 0 \). By juxtaposition of the \( m \) equations of the type (8) we see that:

\[
\begin{pmatrix}
P_{11} & P_{12} & P_{1m} \\
P_{21} & P_{22} & P_{2m} \\
\vdots & \vdots & \vdots \\
P_{m1} & P_{m2} & P_{mm}
\end{pmatrix} = S^{-1} \exp(-\int_0^t \Lambda(u) du) S P_0
\]  

(9)

where \( P_0 \) is a diagonal matrix containing the \( p_j \). For given configurations \( C_j(t) \) and \( C_k(0) \):

\[
\sum_{s=1}^n (P_{s-1} C_j(t)) \, \mathcal{F} \, C_k(0) = \sum_{r_u \in C_j} \sum_{r_w \in C_k} e^{i \mathbf{Q} \cdot \mathbf{r}_u(t)} e^{-i \mathbf{Q} \cdot \mathbf{r}_w(0)}
\]

\[
= ( \sum_{r_u \in C_j} e^{i \mathbf{Q} \cdot \mathbf{r}_u(t)} ) ( \sum_{r_w \in C_k} e^{-i \mathbf{Q} \cdot \mathbf{r}_w(0)} ) = \mathcal{F}_{C_j(t)}^* \mathcal{F}_{C_k(0)}(\mathbf{Q})
\]

where

\[
\mathcal{F}_C(\mathbf{Q}) = \sum_{r_v \in C} e^{-i \mathbf{Q} \cdot \mathbf{r}_v}
\]  

(10)

The thermal averages occurring in equations (4) or (5) can thus be expressed as a sum of terms \( \mathcal{F}_{C_j(t)}^* \mathcal{F}_{C_k(0)}(\mathbf{Q}) \), weighted by their probabilities \( p_{jk}(t) \), i.e. \( \sum_{j,k=1}^m \mathcal{F}_{C_j}^* \mathcal{F}_{C_k}(\mathbf{Q}) p_{jk}(t) \mathcal{F}_{C_k}(\mathbf{Q}) \), where \((j, k)\) run over all possible configurations. Hence it is convenient to introduce the row matrix or vector

\[
[\mathbf{F}(\mathbf{Q})] = [\mathcal{F}_{C_1}^* \mathcal{F}_{C_2}^* \mathcal{F}_{C_3}^* \ldots \mathcal{F}_{C_m}^*](\mathbf{Q})
\]  

(11)
to describe the coherent scattering function as:

\[ S(Q,\omega) = \int_{-\infty}^{\infty} e^{-i\omega t} [F(Q)] S^{-1} \exp(-\int_0^t \Lambda(u)du)SP_0[F(Q)]^\dagger dt \]

\[ = [F(Q)] S^{-1} \Lambda^*(\omega)SP_0[F(Q)]^\dagger \quad (12) \]

\( \Lambda^* \) is the Fourier transform of \( \exp(-\int_0^t \Lambda(u)du) \); \( \dagger \) stands for Hermitian conjugation. It may transpire that equation (12) is rather remote from a Vineyard type of approximation [9].

It must be clearly understood that in our calculations each jump or set of simultaneous jumps must correspond to a change of configuration. The formalism has to be applied with caution if several particles make up a rigid body, as e.g. the D atoms in a CD$_4$ rotor: such totally correlated simultaneous jumps have not been accounted for in the formalism if they lead to the situation that after a "jump" the final configuration is identical to the initial one. This effect could be possibly allowed for in the formalism, but in the case of \( 2\pi/3 \) jumps around the symmetry axes of the CD$_4$ molecule we will end up with only one possible configuration and not very much will be gained by using the present formalism. Let us finally mention that the factorisation of equation (2) obtained in equation (10) can be extended so as to include also the scattering lengths \( b_i \), which suggests that the formalism in terms of configurations also applies to cases with non-identical particles. Several subsets wherein the particles remain indistinguishable may then exist within a configuration.

3. An example: an octagonal tiling model.

Before formulating the second remark of our note we will first illustrate our technique by applying it to a problem of atomic ("phason") hopping in a cluster taken from an octagonal quasiperiodic tiling as described by Kalugin and Katz [10]. Three atoms can move as shown in figure 1a. Inside the tiling we perceive assemblies of three tiles that look as the drawing of a cube in perspective (e.g. inside the hexagon LOGHAB). This is a consequence of the fact that this quasiperiodic tiling model is obtained by projection from a 4D hypercubic tiling. The projection of the 4D hypercube onto \( \mathbb{R}^2 \) is shown in figure 1b. An atomic jump corresponds to a change in perspective in a cube (and is called a phason). After eight moves we get back to the initial configuration but the three atoms in I, L and O have undergone a cyclic permutation. The three atoms diffuse on the small octagon IJKLMNOP of figure 1b, but in a strongly correlated way. Such toy models are thought to give the essence of the problem of atomic jumps in quasicrystals. On a larger quasiperiodic tiling they can lead to long-range diffusion and complicated cooperative dynamics. The point is that with the present technique we might get a first grasp on such complicated correlated systems. In icosahedral AlFeCu there exist probably "floating clusters" of 7 Cu atoms on a dodecahedron [11]. The rule of the game is here that pairs of atoms should never occupy first neighbour sites with respect to each other. Moreover, they should never occupy symmetrically opposite sites on the dodecahedron. Quasielastic coherent scattering from Cu atoms has been observed in this system [12], which justifies a study of the problem evoked. There are 320 different configurations meeting the first condition. This number is further reduced to 100 by the second one. Without the theorem the rank of the jump matrix to be considered would be much higher, since we would have to allow for all possible permutations of the particles that can occur within a configuration, and the rank could be \( 100 \times 7! \) in the worst case that all of them are actually allowed. Just finding out which permutations have to be accounted for constitutes already a major effort in its own right. We just mention this example to indicate how the new method presents a definite advantage.
over the older ones. From now on we will deal only with the much simpler calculation of figure 1. As can be seen from inspection of figure 1 there are only 8 indistinguishable configurations. If we assume that the transition probability between two clusters is always the same \((1/\tau)\) the rate equations become formally identical to those for the motion of a single particle on a regular octagon, as described by Bée [2], who gives the more general solution for a single particle on a regular \(n\)-gon:

\[
\frac{dP_j}{dt} = \frac{1}{\tau} P_{j-1} - \frac{2}{\tau} P_j + \frac{1}{\tau} P_{j+1}
\]

(13)

Fig. 1. — Left: model of three correlated particles diffusing on an octahedron. Right: 2D projection of a 4D hypercube which helps to visualise the octagon of sites visited by the particles (IJKLMNOP)

Here \(P_j(t)\) is the probability to find the particle in site \(j\) at time \(t\). Keeping in mind the caveat about the different meanings of the quantities involved (as explained above), we can exploit this formal identity and apply immediately the results of reference [2] to our cluster transition probabilities. The matrix to be diagonalised is thus

\[
\frac{1}{\tau} (-\delta_{j,k-1} + 2\delta_{j,k} - \delta_{j,k+1})
\]

(14)

It has the topology of the problem of the phonons of a linear chain of masses \(\mu\) with uniform distances \(a\), spring constants \(\kappa\) and cyclic boundary conditions. This makes it possible to map the problem of the transition probabilities between the clusters on a problem of phonons on a periodic lattice. The symmetry can be expressed as a translational invariance where the coefficients of the basis vectors of the lattice are integers modulo \(J \in \mathbb{Z}\) (e.g. the diffusion of a particle on a cube is described by the same equations as for a cubic lattice if the coefficients are taken modulo 2). In this way one can immediately postulate the eigenvalues and eigenvectors based on the Bloch theorem, and the diagonalisation of the matrix becomes simple. This comes down to postulating:

\[
P_\tau = U_\tau e^{i\mathbf{q} \cdot \mathbf{r}}
\]

(15)
A NOTE ON QUASIELASTIC NEUTRON SCATTERING

\[ M = M + 5 \]

\[ Q = M + 5 \]

\[ Q^2 = 2m + \alpha \]

\[ P_m Q^2(b) \]

The part in \( U_q \) leads to rate equations and eigenvalues. The exponential part leads to the eigenvectors. For the linear chain this yields:

\[ S_{kj} = \frac{1}{\sqrt{m}} \exp(-i \frac{2\pi}{m}(k-1)(j-1)) \]

\[ \Lambda_{jk} = \frac{4}{\tau} \sin^2\left(\frac{\pi}{m}(j-1)\right) \delta_{kj} \]

\[ P_0 = 1_{m \times m} \]  \hfill (16)

Identification with the phonon problem is obtained by

\[ \frac{2\pi(j-1)}{m} \rightarrow qa; \quad \frac{1}{\tau} \rightarrow \frac{\kappa}{\mu}; \quad \Lambda_{jk} \rightarrow \omega^2 \]  \hfill (17)

We number the clusters as in figure 1, i.e. \( \text{ILO} \rightarrow C_1, \text{LOJ} \rightarrow C_2, \text{OHJ} \rightarrow C_3, \ldots \). We assign vectors \( e_i = (\cos(\pi(i-1)/4), -\sin(\pi(i-1)/4)) \) to the positions of the sites \( \text{IJKLMNOP} \). The 8 different clusters \( C_j \) are then given by triplets\( (e_1@\text{I}, e_1@\text{J}, e_1@\text{P}) \), where here again the sums in the indices have to be taken modulo 8. E.g. for \( C_1 \) we find a triplet \( (e_1, e_4, e_7) \).
The probability that at time $t$ the system has taken up the configuration $C_j$ is given by the quantities $P_j$ obeying the set of differential equations (13). As clusters $C_j$ and $C_{j+1}$ have the sites $e_{13j}$ and $e_{13(j+1)}$ in common the transition from the first to the second one is achieved by a jump from the site $e_{13j}$ to the site $e_{13(j+2)}$. These conventions lead to:

$$\mathcal{F}_{C_j}(Q) = \exp(-iQ \cdot e_{13j}) + \exp(-iQ \cdot e_{13j'}) + \exp(-iQ \cdot e_{13(j+1)})$$

$$\left(\Lambda^*(\omega)\right)_k = \frac{1}{\pi \omega^2 + \Gamma_j^2} \delta_{kj}; \quad \Gamma_j = \frac{4}{\tau} \sin^2\left(\frac{\pi}{8}(j-1)\right)$$

Calculation from equation (12) of $S(Q, \omega)$ is now straightforward, be it tedious. The details are outlined in the Appendix. The final results are summarised in table I and figures 3 and 4.

![Graph](attachment:graph.png)

Fig. 3. — Coherent structure factors as listed in table I for the various contributions to the energy line-shape. $S_{el}(Q)$ is the sum of the structure factors as described in the text.

4. Incoherent scattering

In the previous example the problem of incoherent scattering would require the use of $24 \times 24$ matrices, which underlines the power of the method. In fact for incoherent scattering the rank of the matrix is $nm$ due to the fact that only one particle has been tagged and $(n-1)$ particles remain indistinguishable. This can be easily understood as follows. It suffices [3] to replace each cluster in paragraph 2 by $n$ clusters which only differ from one another by the position of the tagged particle in the cluster. One then has to write the jump matrix for the transition probabilities between $nm$ tagged clusters. Even this can be a considerable simplification in comparison to the classical approach, where it is customary to try to write down differential equations describing the single-particle jumps. The previous example clearly shows the complications this entails, since the jump probability for one particle depends on
Fig. 4. — Total compounded coherent quasi-elastic signal \( S(Q, \omega) \) without the elastic peak as a function of \( Q \) and \( \omega \). A 3D-plot (left) and a contour map (right) are shown. The dashed line on the contour map shows the \( (Q, \omega) \) values where the intensity is at half the value of the maximum at \( (Q,0) \). It is clear that the signal is largely dominated by the first Lorentzian in Table I, such that the FWHM is almost \( Q \)-independent.

Table I. — Components of the total structure factor \( S(Q, \omega) \) for atomic hopping on the octagonal tiling in the model of figure 1 (average over a powder sample without texture). The Lorentzians \( \Lambda \) are specified by their HWHM \( \Gamma \).

<table>
<thead>
<tr>
<th>Line shape</th>
<th>Structure factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \delta )</td>
<td>( \frac{9}{8} \left( 1 + 2j_0(QD_1) + 2j_0(QD_2) + 2j_0(QD_3) + j_0(QD_4) \right) )</td>
</tr>
<tr>
<td>( \Lambda(\frac{2 + \sqrt{2}}{\tau}) )</td>
<td>( \frac{1}{4} \left( 3 + 2\sqrt{2} \right) \left( 1 - \sqrt{2}j_0(QD_1) + \sqrt{2}j_0(QD_3) - j_0(QD_4) \right) )</td>
</tr>
<tr>
<td>( \Lambda(\frac{2}{\tau}) )</td>
<td>( \frac{1}{4} \left( 1 - 2j_0(QD_2) + j_0(QD_4) \right) )</td>
</tr>
<tr>
<td>( \Lambda(\frac{2 + \sqrt{2}}{\tau}) )</td>
<td>( \frac{1}{4} \left( 3 - 2\sqrt{2} \right) \left( 1 + \sqrt{2}j_0(QD_1) - \sqrt{2}j_0(QD_3) - j_0(QD_4) \right) )</td>
</tr>
<tr>
<td>( \Lambda(\frac{4}{\tau}) )</td>
<td>( \frac{1}{8} \left( 1 - 2j_0(QD_1) + 2j_0(QD_2) - 2j_0(QD_3) + j_0(QD_4) \right) )</td>
</tr>
</tbody>
</table>

the issue if another particle (the preceding one) has already jumped. It is in fact hard to imagine how one could solve this problem without eventually falling back onto a description in terms of configurations, possibly allowing (unnecessarily) for all allowed permutations of the particles. Hence even in this less favourable case the new approach presents a significant simplification. The incoherent case will of course require the use of single-particle structure
Fig. 5. — Incoherent structure factors as listed in table II for the various contributions to the energy line-shape. The structure factor $S_9$ is omitted as it is zero.

Fig. 6. — Total compounded incoherent quasi-elastic signal ($S_{inc}(Q, \omega)$ without the elastic peak) as a function of $Q$ and $\omega$. Three dimensional plot and contour map. The dashed line on the contour map shows again the location of the points where the intensity is at half the maximum value at $\omega = 0$.

factors only, instead of the more complicated quantities $F$. In the Appendix we derive the incoherent scattering function corresponding to the problem of the octagonal tiling described
in paragraph 3. The final results are summarised in table II and figures 5 and 6. The jump equations are obtained by using a description in terms of 24 configurations. Since the particles cannot leap-frog on the tiling, this is also the number of all allowed configurations, i.e. there is no simplification here by a presence of indistinguishable permutations.

Table II. — Components of the incoherent structure factor $S_{\text{inc}}(Q, \omega)$ for the problem of atomic hopping on an octagonal tiling illustrated in figure 1 (case of a powder sample without texture). The Lorentzians $\Lambda$ are characterised by their HWHM $\Gamma$. The structure factor corresponding to $\delta(\omega)$ is also called elastic incoherent structure factor (EISF). The structure factor $S_0$ is not listed as it is zero.

<table>
<thead>
<tr>
<th>Line shape</th>
<th>Structure Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta$</td>
<td>$3(1 + 2j_0(QD_1) + 2j_0(QD_2) + 2j_0(QD_3) + j_0(QD_4))/8$</td>
</tr>
<tr>
<td>$\Lambda(2\cdot\sqrt{2+\sqrt{3}} \tau)$</td>
<td>$(3 + 2\sqrt{2+\sqrt{3}} + \sqrt{3})(1 + \sqrt{2}j_0(QD_1) - \sqrt{2}j_0(QD_3) - j_0(QD_4))/12$</td>
</tr>
<tr>
<td>$\Lambda(2\cdot\sqrt{3} \tau)$</td>
<td>$(2 + \sqrt{3})(1 - 2j_0(QD_2) + j_0(QD_4))/6$</td>
</tr>
<tr>
<td>$\Lambda(2\cdot\sqrt{2} \tau)$</td>
<td>$(3 + 2\sqrt{2})(1 - \sqrt{2}j_0(QD_1) + \sqrt{2}j_0(QD_3) - j_0(QD_4))/12$</td>
</tr>
<tr>
<td>$\Lambda(1 \tau)$</td>
<td>$[1 - 2j_0(QD_1) + 2j_0(QD_2) - 2j_0(QD_3) + j_0(QD_4)]/3$</td>
</tr>
<tr>
<td>$\Lambda(2\cdot\sqrt{2-\sqrt{3}} \tau)$</td>
<td>$(3 + 2\sqrt{2-\sqrt{3}} - \sqrt{3})(1 - \sqrt{2}j_0(QD_1) + \sqrt{2}j_0(QD_3) - j_0(QD_4))/12$</td>
</tr>
<tr>
<td>$\Lambda(2 \tau)$</td>
<td>$[1 - 2j_0(QD_2) + j_0(QD_4)]/12$</td>
</tr>
<tr>
<td>$\Lambda(2+\sqrt{2-\sqrt{3}} \tau)$</td>
<td>$(3 - 2\sqrt{2-\sqrt{3}} - \sqrt{3})(1 + \sqrt{2}j_0(QD_1) - \sqrt{2}j_0(QD_3) - j_0(QD_4))/12$</td>
</tr>
<tr>
<td>$\Lambda(2+\sqrt{2} \tau)$</td>
<td>$(3 - 2\sqrt{2})(1 + \sqrt{2}j_0(QD_1) - \sqrt{2}j_0(QD_3) - j_0(QD_4))/12$</td>
</tr>
<tr>
<td>$\Lambda(2+\sqrt{3} \tau)$</td>
<td>$(2 - \sqrt{3})(1 - 2j_0(QD_2) + j_0(QD_4))/6$</td>
</tr>
<tr>
<td>$\Lambda(2+\sqrt{2+\sqrt{3}} \tau)$</td>
<td>$(3 - 2\sqrt{2+\sqrt{3}} + \sqrt{3})(1 - \sqrt{2}j_0(QD_1) + \sqrt{2}j_0(QD_3) - j_0(QD_4))/12$</td>
</tr>
<tr>
<td>$\Lambda(4 \tau)$</td>
<td>$[1 - 2j_0(QD_1) + 2j_0(QD_2) - 2j_0(QD_3) + j_0(QD_4)]/24$</td>
</tr>
</tbody>
</table>
5. Diagrams as matrix representations.

Calculations of scattering functions often lead to boring lengthy calculations to cast the problem into the Jordan form (6) and powder averaging of (12) generally introduces Bessel functions, which make the final result look very impressive. From the use of the Bloch theorem in the previous example it may have become clear that one can often simplify the calculations considerably by exploiting all the symmetry properties of the problem. The 8 Bloch waves are in a sense symmetry adapted functions. Very often the mere notation of the matrix $M$ in the form of a square already will conceal us some of the properties. We therefore propose to write down the matrix in the form of a so-called Schlegel diagram as shown in figure 2a for the matrix that corresponds to the differential equations for the diffusion of a particle on an icosahedron $T$. (A Schlegel diagram of an object is a drawing that gives its topology, i.e. the connections between its vertices). The diagram corresponds to one line $i$ of this matrix $M$. In each vertex $j$ of the diagram we put the term $M_{ij}$, i.e. by writing $-5$ in A and $+1$ in B, C, D, E and F in figure 2a we express

$$\frac{dP_A}{dt} = -5P_A + P_B + P_C + P_D + P_E + P_F$$

(19)

However, apart from the labelling with A, B, C,... all 12 diagrams will be the same due to symmetry. Thus, figure 2a represents, in a sense, the whole matrix $M$. We now consider the matrix $Q = 5\Pi_{12 \times 12} + M$, which is presented by putting a zero in A and a 1 in B, C, D, E, and F. To calculate $Q^n$, we just have to give a rule to calculate $TQ$ for a matrix $T$ with the same symmetry so that it can be represented on the same type of Schlegel diagram. Let us consider a point P on line A of matrix $T$, i.e. a point P on drawing A of matrix $T$. This point corresponds to the element $T_{AP}$. We now want the value for P on drawing A of $TQ$, i.e. $(TQ)_{AP} = \sum T_{AJ} Q_{JP}$. The values of $T_{AJ}$ can be found in the points J of the corresponding drawing A of matrix $T$. Of the elements $Q_{JP}$ only those values of J that correspond to the neighbors of P will have a non-zero contribution (equal to 1), such that:

$$\sum_{J \in \mathcal{N}(P)} T_{AJ} Q_{JP} = \sum_{J \in \mathcal{N}(P)} T_{AJ}$$

(20)

where $\mathcal{N}(P)$ is the set of the first neighbors of P; i.e. to find the number to put on vertex P of diagram A of $TQ$, we just have to sum all numbers on the neighbors of P on diagram A of $T$. This is child's play as illustrated in figure 2b for $Q^2$. It is much less laborious than the standard way of performing matrix calculations since we have to calculate only one line and one does not have to strain one's eyes to ensure that the right elements are multiplied. Moreover the notation is much quicker than writing down a square of $n^2$ elements. Figure 2b shows how $Q^2$ can be rewritten as a sum. The first diagram corresponds to $2 \times 12 \times 12$, a $12 \times 12$ matrix containing numbers 2 everywhere. The second diagram shows that if we index the point corresponding to $-r_A$ by index($A$) + 6 then the diagram can be written under block form as

$$\begin{pmatrix} 3\Pi_{6 \times 6} & -2\Pi_{6 \times 6} \\ -2\Pi_{6 \times 6} & 3\Pi_{6 \times 6} \end{pmatrix}$$

(21)

which we will further note down as $\alpha$. As $\ell \alpha = \beta$ and $\alpha$ is very easy to diagonalize it just takes a few lines to solve $Q^{2n}$ and $Q^{2n+1}$, and thus also $\exp(M)$ as $\exp(-5) \exp(Q)$. This shows how this diagrammatic method allows us to calculate $\exp(M)$ in a few lines without reducing $M$ to the Jordan form. To solve the problem of a particle diffusing on a dodecahedron one has to calculate up to $Q^4$, to find the general formula for $Q^n$. Of course each case will require some
ad hoc skill in summing the Taylor series, such that the method at this stage of development is not as systematic as an approach based on group theory, but it may constitute in several cases a genuine short-cut for the calculations. In fact the matrices of the type \( \mathbf{A} \) are bound to occur sooner or later as they represent the infinite time solution where all the memory of the initial conditions has been lost. This is intimately related to the fact that in a finite system we will find trajectories that are loops.

Appendix 1.

Further details on the calculation of the scattering functions for the octagonal tiling.

In this Appendix we will give some more details on the calculations for the total scattering function corresponding to the example of paragraph 3. First we show that \( S \) defined by equation (16) obeys \( SS^* = 1 \), such that \( S^{-1} = S^* \). In fact:

\[
\sum_{j=1}^{m} S_{kj} S_{jl} = \frac{1}{m} \sum_{j=1}^{m} \exp\left(-\frac{i2\pi}{m}(k-1)(j-1)\right) \exp\left(\frac{i2\pi}{m}(j-1)(l-1)\right) = \frac{1}{m} \sum_{j=1}^{m} \exp\left(-\frac{i2\pi}{m}(k-l)(j-1)\right) = \delta_{kl} \tag{A1}
\]

Further \( SAS^* \) yields the matrix \( M \) defined in equation (13):

\[
\sum_{j=1}^{m} \sum_{l=1}^{m} S_{kj} A_{jl} S_{lh}^* =
\]

\[
= \frac{1}{m} \sum_{j,l} \exp\left(-\frac{i2\pi}{m}(k-1)(j-1)\right) \frac{4}{\tau} \sin^2\left(\frac{\pi}{m}(j-1)\right) \delta_{jl} \exp\left(\frac{i2\pi}{m}(l-1)(h-1)\right) = \frac{1}{m} \sum_{l=1}^{m} \exp\left(-\frac{i2\pi}{m}(k-h)(l-1)\right) \frac{4}{\tau} \sin^2\left(\frac{\pi}{m}(l-1)\right) \exp\left(\frac{i2\pi}{m}(l-1)(h-1)\right) = \sum_{l=1}^{m} \left( \frac{2}{m} \exp\left(-\frac{i2\pi}{m}(k-h)(l-1)\right) - \frac{1}{m} \exp\left(-\frac{i2\pi}{m}(k-h+1)(l-1)\right) \right) - \frac{1}{m} \exp\left(-\frac{i2\pi}{m}(k-h-1)(l-1)\right) = 2\delta_{kh} - \delta_{k,h-1} - \delta_{k,h+1} \tag{A2}
\]

where we have expressed the sine function in terms of exponentials. Let us now calculate the elements \( p_{kh} \) of the matrix \( \exp(-Mt) \). We assign the probability \( 1/m \) to each initial condition:

\[
p_{kh}(t) = \frac{1}{m} \sum_{j,l} S_{kj} (\exp(-\Lambda t))_{jl} S_{lh}^* = \frac{1}{m^2} \sum_{j,l} \exp\left(-\frac{i2\pi}{m}(k-1)(j-1)\right) \frac{4}{\tau} \sin^2\left(\frac{\pi}{m}(j-1)\right) \delta_{jl} \exp\left(-\frac{4t}{\tau} \sin^2\left(\frac{\pi}{m}(j-1)\right)\right) \frac{1}{m} \sum_{j,l} \exp\left(-\frac{i2\pi}{m}(l-1)(h-1)\right)
\]

\[ \frac{1}{m^2} \sum_{k=1}^{m} \exp(-\frac{i2\pi}{m}(k-h)(l-1)) \exp(-\frac{4\pi}{\tau} \sin^2(\frac{\pi}{m}(l-1))) \]  
(A3)

After Fourier transform the terms \( \exp(-\frac{4\pi}{\tau} \sin^2(\frac{\pi}{m}(l-1))) \) will give rise to the Lorentzians \( \Lambda_l^*(\omega) \) defined in equations (16) and (18). It is convenient to calculate the structure factor of each Lorentzian separately. The prefactor of the \( l \)-th exponential in the total scattering function \( \sum_{h,k} \mathcal{F}_{c_k}(Q)p_{kh}(t)\mathcal{F}^*_c(Q) \) is:

\[ \frac{1}{m^2} \sum_{k=1}^{m} \sum_{h=1}^{m} \mathcal{F}_{c_k}(Q) \exp(-\frac{i2\pi}{m}(k-h)(l-1))\mathcal{F}^*_c(Q) = \]
\[ = \left( \sum_{k=1}^{m} \frac{1}{m} \mathcal{F}_{c_k}(Q) \exp(-\frac{i2\pi}{m}k(l-1)) \right) \left( \sum_{h=1}^{m} \frac{1}{m} \mathcal{F}_{c_h}(Q) \exp(-\frac{i2\pi}{m}h(l-1)) \right)^* \]
\[ = \left| \frac{1}{m} \sum_{k=1}^{m} \mathcal{F}_{c_k}(Q) \exp(-\frac{i2\pi}{m}k(l-1)) \right|^2 = |U_l(Q)|^2 \]  
(A4)

By introducing \( x_l = \exp(-\frac{i2\pi}{m}(l-1)) \) the terms \( U_l(Q) \) can be rewritten as:
\[ U_l(Q) = \frac{1}{m} \sum_{k=1}^{m} \mathcal{F}_{c_k}(Q)(x_l)^k. \]

By grouping all the terms which contain \( \exp(-iQ \cdot e_j) \) inside this expression we obtain:
\[ \frac{1}{m} \frac{1 + x_l + x_l^2}{x_l} x_l^{3(j-1)} \exp(-iQ \cdot e_j) \]  
(A5)

In our case \( n = m = 8 \) such that \( j \) runs from 1 to 8. From formula (A5) it follows that \( U_l(Q) \) is the Fourier transform of the distribution:
\[ \frac{1}{8} \frac{1 + x_l + x_l^2}{x_l} \sum_{j=1}^{8} (x_l)^{3(j-1)} \delta(r - e_j) \]  
(A6)

For \( l = 1 \), this is just the Fourier transform of the octagon IJKLNMOP normalised by a factor 3/8, which is a very intuitive result. For higher values of \( l \) the terms (A6) can be considered as Fourier transforms of higher order moments. The \( l = 1 \) term in \( S(Q, \omega) \) is thus \( \frac{3}{64} S(Q)_{\text{oct}}. \delta(\omega). \)

We have \( x_1 = 1 \) and \( x_l^{3(j-1)} = \exp(i \frac{\pi}{4}(l-1)3(j-1)) = x_{L(l,j)}^* \), where \( L(l, j) \) is defined by \( L(l, j) - 1 \equiv (l-1)3(j-1)(\text{mod}8) \). The values of \( L(l, j) \) are listed in table III for convenience.

Furthermore, \( x_L^* x_K = x_{L-K+1}^* \). The product \( U_l^* U_l \) is given by:
\[ \frac{1}{64} \frac{1 + x_l + x_l^2}{x_l} \left| \sum_{j,k} x_l^{3(j-1)} x_l^{3(k-1)} \exp(iQ \cdot (e_j - e_k)) \right|^2 \]  
(A7)

There are 64 combinations \((j, k)\). The 8 combinations with \( j = k \) give rise to terms under the sum that are equal to 1. The 16 combinations with \( |j - k| = 1 \) correspond to vectors \( e_j - e_k \) that are edges of the octagon and have a length \( D_1 = \sqrt{2} - \sqrt{2}R \), where \( 2R \) is the diameter of the octagon IJKLNMOP. The 16 combinations with \( |j - k| = 2 \) correspond to a diagonal with a length \( D_2 = \sqrt{2}R \). The 16 combinations with \( |j - k| = 3 \) correspond to a diagonal with a length \( D_3 = \sqrt{2} + \sqrt{2}R \) and finally the 8 combinations with \( |j - k| = 4 \) correspond to a diameter of the octagon \( (D_4 = 2R) \). In all cases with \( j \neq k \) the term \((k, j)\) is the complex conjugate of the term \((j, k)\) and gives rise to the same type of distance. In total we have
Table III. — Values of $L(j, l)$; see text.

<table>
<thead>
<tr>
<th>j</th>
<th>1 2 3 4 5 6 7 8</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1 1 1 1 1 1 1 1</td>
</tr>
<tr>
<td>2</td>
<td>1 4 7 2 5 8 3 6</td>
</tr>
<tr>
<td>3</td>
<td>1 7 5 3 1 7 5 3</td>
</tr>
<tr>
<td>4</td>
<td>1 2 3 4 5 6 7 8</td>
</tr>
<tr>
<td>5</td>
<td>1 5 1 5 1 5 1 5</td>
</tr>
<tr>
<td>6</td>
<td>1 8 7 6 5 4 3 2</td>
</tr>
<tr>
<td>7</td>
<td>1 3 5 7 1 3 5 7</td>
</tr>
<tr>
<td>8</td>
<td>1 6 3 8 5 2 7 4</td>
</tr>
</tbody>
</table>

$1(j = k) + 4(|j - k| = 1) + 4(|j - k| = 2) + 4(|j - k| = 3) + 4(|j - k| = 4)$ independent terms of the form:

$$A \exp(iQ \cdot (e_j - e_k)) + \text{complex conj.} =$$

$$= 2 \text{Re}(A) \cos(Q \cdot (e_j - e_k)) - 2 \text{Im}(A) \sin(Q \cdot (e_j - e_k))$$

(A8)

In the structure factors corresponding to $D_1$, $D_2$ and $D_3$ we have in fact a further reduction of the number of independent terms by a factor of 2, due to symmetry. The large number of independent terms makes the expression of $S(Q, \omega)$ cumbersome. Fortunately powder averaging turns all the terms $\cos(Q \cdot (e_j - e_k))$ into $j_0(QD_{j-k})$ and the terms $\sin(Q \cdot (e_j - e_k))$ into zeros (for $j \neq k$), which makes the final expression more tractable. It is given in terms of its various contributions in table I. Following Béé [2] we show in figure 3 how these structure factors vary as a function of $Q$. In figure 4 we show the variation of the total quasi-elastic signal as a function of $Q$ and $\omega$. As cross-check one may calculate $\lim_{\tau \to \infty} S(Q, \omega)$. As in the sense of distributions $\lim_{\Gamma \to 0} \Gamma/\pi(\omega^2 + \Gamma^2) = \delta(\omega)$, $S(Q, \omega)$ should tend to $S(Q) \delta(\omega)$, where $S(Q)$ is the sum of the structure factors listed in table I, i.e. $3 + 2j_0(QD_2) + 4j_0(QD_3)$. On the other hand $S(Q, \omega)$ should tend to $S(Q) \delta(\omega)$, with $S(Q)$ the powder average of $S(Q) = \mid \mathcal{F}_{C_1}(Q) \mid^2$. As $C_1$ is the triplet $(e_1, e_4, e_7)$, we find for $S(Q)$:

$$3 + 2[\cos((e_4 - e_1) \cdot Q) + \cos((e_7 - e_1) \cdot Q) + \cos((e_4 - e_7) \cdot Q)]$$

(A9)

After powder averaging this leads indeed to the result announced.

A final remark is due here as to the choice of the clusters. We claimed that the clusters were to be taken as the triplets of jumping atoms such as ILO, LOJ etc. But with equal rights we could have considered the clusters as being built up from 11 atoms, viz. the triplet of jumping atoms completed by the large frame octagon $O$ of the fixed atoms on sites ABCDEFGH. Each factor $\mathcal{F}_{C_j}(Q)$ would then have to be replaced by $\mathcal{F}_{C_j}(Q) + \vartheta$, with $\vartheta = \sum_{R_i} e_i \exp(-iQ \cdot R_i)$. In the final expression corresponding to equation (12) the quantity $[F(Q)]$ has then to be replaced by $[F(Q)] + (1, 1, . . , 1) \vartheta$. Does this mean that the non moving parts of the surroundings could change the total scattering function by an interference contribution? Fortunately the jump matrices of the type $M$ all have the conservation law property $(1, 1, . . , 1) M = (0, 0, . . , 0)$, thus also $(1, 1, . . , 1) M^2 = (0, 0, . . , 0)$ and by Taylor expansion $(1, 1, . . , 1)(\exp(Mt) - 1) = (0, 0, . . , 0)$, such that the inelastic scattering corresponding
to equation (12) is independent of the choice of the clusters and that our specific choice of minimal clusters is justified.

Let us call the particle that is in I when we are in configuration 1 of figure 1 the first particle. In each of the eight clusters considered for the case of coherent scattering we can encounter this first particle in three possible sites, such that we have to consider 24 configurations to deal with the incoherent scattering function. The 24 $\times$ 24 jump matrix is again of the form given in equations (13, 14) and its diagonalisation required for the solution of the rate equations is given by equations (16) with $m = 24$. This should lead to an incoherent scattering function as in equation (12) with the matrix $[\hat{F}(Q)]$ replaced by:

$$[\exp(iQ \cdot e_1), \exp(iQ \cdot e_4), \exp(iQ \cdot e_4), \exp(iQ \cdot e_7),..$$

$$.. \exp(iQ \cdot e_5), \exp(iQ \cdot e_1), \exp(iQ \cdot e_1)]$$

(A10)

This expression reflects the fact that the first particle is in I inside cluster 1, remains in L in clusters 2, 3 and 4, in O in clusters 5, 6 and 7, ... and returns to I in clusters 23 and 24. Hence the first particle is at site $e_j$ within clusters $3(j - 2) + v$, with $v = 2, 3, 4$ and the contribution from the terms with initial position $e_j$ and position $e_k$ at time $t$ to the intermediate scattering function $I(Q, t)$ is given by:

$$\exp(-iQ \cdot e_j)(\sum_{v=2}^{4} \sum_{w=2}^{4} \exp(2\pi i(v-2)u;3(k-2)+w(t)) \exp(iQ \cdot e_k) =$$

$$= \frac{1}{(24)^2} \exp(-iQ \cdot (e_j - e_v)) \sum_{l=1}^{24} \exp(-i\frac{\pi}{4}(j - k)(l - 1)) \exp(-\frac{4t}{\tau} \sin^2(\frac{\pi}{24}(l - 1)))$$

$$\times [3 + 4 \cos(\frac{\pi}{12}(l - 1)) + 2 \cos(\frac{\pi}{6}(l - 1))]$$

(A11)

Here we have replaced the probabilities $p$ by their expressions given by equations (16) in the same way as was done to obtain equations (A3). Each initial configuration has been assigned an equal probability $1/24$ here. The last line of equation (A11) summarises the fact that among the nine combinations $(v, w)$, three have $|v - w|$ equal to 0, 4 equal to 1 and 2 equal to 2. For each value of $l$ we have a corresponding Lorentzian (or Dirac $\delta$) $\Delta_l^I(\omega)$, for which one should calculate the structure factor. The calculation is again simplified if we are only interested in powder averages, such that terms can be grouped according to the value of $|j - k|$ and the factors $\exp(-iQ \cdot (e_j - e_k))$ reduce to spherical Bessel functions $j_0(QD_{|j-k|})$. For a given value of $l$ we find terms:

$$[3 + 4 \cos(\frac{\pi}{12}(l - 1)) + 2 \cos(\frac{\pi}{6}(l - 1))]$$

$$\times [8 + 16j_0(QD_1) \cos(\frac{\pi}{4}(l - 1)) + 16j_0(QD_2) \cos(\frac{\pi}{2}(l - 1))$$

$$+ 16j_0(QD_3) \cos(\frac{3\pi}{4}(l - 1)) + 8j_0(QD_4) \cos(\pi(l - 1))]$$

$$\times [\Delta_l^I(\frac{-4}{\tau} \sin^2(\frac{\pi}{24}(l - 1)))]$$

$$\times \frac{3}{(24)^2}$$

(A12)

The factor 3 in the last line of equations (A12) is caused by the presence of three particles. The final expression is further compacted by realising that contributions from $l$ and $26-l(mod24)$ are
identical, such that it can be written in terms of 12 Lorentzians and one Dirac \( \delta \)-distribution. The Lorentzian with width \( 3/\tau \) (from the term with \( l = 9 \)) turns out to have a zero structure factor, so that eventually we end up with 11 Lorentzians and one \( \delta \). As a cross-check one may calculate the total incoherent structure factor which should be the constant 3. The results are summarised in table II and figures 5 and 6.

Appendix 2.

Further details of the calculation of \( \exp(M) \) by means of diagrams.

From the diagrams in figure 2 it follows: \( (M + 5)^2 = \alpha + 2\mathbf{m} \).

We can use this identity to give a general expression for \( (M + 5)^{2n} \). It is easily verified by block diagonalisation in equation (21) that

\[
\alpha^n = \frac{1}{2} \begin{pmatrix} (5^n + 1) \mathbf{I} & (-5^n + 1) \mathbf{I} \\ (-5^n + 1) \mathbf{I} & (5^n + 1) \mathbf{I} \end{pmatrix}
\]

(A13)

One can show then that \( \mathbf{m} \alpha^n = \mathbf{m} \alpha^n = \mathbf{m} \). Furthermore \( \mathbf{m}^2 = (12)^{-1} \mathbf{m} \). The binomial expansion of \( (M + 5)^{2n} \) yields then

\[
\alpha^n + \frac{1}{12} \sum_{j=1}^{n} \alpha^{n-j} \begin{pmatrix} n \\ j \end{pmatrix} 24^j \mathbf{m} = \alpha^n + \frac{1}{12} ((25)^n - 1) \mathbf{m}
\]

(A14)

We now introduce the notation \( \sqrt{\alpha} \) given by

\[
\sqrt{\alpha} = \begin{pmatrix} \tau \mathbf{I} & (1 - \tau) \mathbf{I} \\ (1 - \tau) \mathbf{I} & \tau \mathbf{I} \end{pmatrix}
\]

(A15)

where \( \tau \) stands for the golden mean \( (1 + \sqrt{5})/2 \). In fact \( \sqrt{\alpha} \) has \( \alpha \) as its square. Expression (A15) is also obtained by block diagonalisation of equation (21). The terms \( 2n \) in the Taylor expansion can thus be summed to yield

\[
\text{Ch}(M + 5) = \text{Ch}(\sqrt{\alpha}) + \frac{1}{12} (\text{Ch}(5) - \text{Ch}(1)) \mathbf{m}
\]

(A16)

Here the term \( \text{Ch}(\sqrt{\alpha}) \) can be calculated from the blockdiagonal form of \( \alpha \). Similar calculations on the terms \( (2n + 1) \) yield

\[
\text{Sh}(M + 5) = (\sqrt{\alpha})^{-1} \text{Sh}(\sqrt{\alpha})(Q + 5) + \frac{1}{12} (\text{Sh}(5) - 5 \text{Sh}(1)) \mathbf{m}
\]

(A17)

By considering the partial sums in the Taylor expansion of \( \exp(M + 5) \), it becomes clear that \( \exp(M + 5) \) is the sum of expressions (A16) and (A17). As the matrices \( Q \) and \( 5 \mathbf{I} \) commute, \( \exp(M) = \exp(Q) \exp(-5) \) such that the final result for \( \exp(M) \) can be easily derived. Although the present calculation requires more skill than a brute force procedure by diagonalisation of \( M \), it remains much more tractable than the use of page filling 12 \( \times \) 12 matrices. In the case of the diffusion of a particle on a dodecahedron where the rank of the matrices is 20, this becomes even more important. Of course the calculation of \( \exp(M) \) is only the first step in the calculation of the scattering function, which has to proceed further by the calculation of the
structure factors followed by thermal and powder averaging as outlined in the preceding part of the Appendix.

We would like to end by mentioning a not directly related but amusing property of the connectivity matrices \( Q \). For any lattice \( \mathbb{L} \) one can define a matrix \( Q(\mathbb{L}) \) such that \( (Q(\mathbb{L}))_{ij} = 1 \) if sites \( i \) and \( j \) are connected, (i.e. are first neighbours on \( \mathbb{L} \)), and \( (Q(\mathbb{L}))_{ij} = 0 \) if they are not. Then the element \( ((Q(\mathbb{L}))^k)_{ij} \) of the \( k \)-th power of \( Q(\mathbb{L}) \) counts the number of different (non self-avoiding) walks of length \( k \) between sites \( i \) and \( j \). (It is thus possible to come back to previous positions). This can be verified on the diagram for \( Q^2 \) in figure 2 : there are five ways to go from point A back to A in two steps, viz. ABA, ACA, ADA, AEA and AFA; there are two ways to go from A to C in two steps, viz. ABC and ADC. Using the Bloch theorem it is extremely easy to diagonalise the connectivity matrix of a \( D \)-dimensional hypercubic lattice with cyclic boundary conditions at distance \( L \), (i.e. \( \mathbb{L}^{(D)}_L = ([0, L - 1] \cap \mathbb{Z})^D \)), and thus to calculate its \( k \)-th power. In fact :

\[
\begin{pmatrix}
\exp(i\mathbf{q} \cdot \mathbf{R}_1) \\
\exp(i\mathbf{q} \cdot \mathbf{R}_2) \\
. \\
. \\
\exp(i\mathbf{q} \cdot \mathbf{R}_N)
\end{pmatrix}
= 2 \sum_{i=1}^{D} \cos(q \cdot \mathbf{e}_i)
\begin{pmatrix}
\exp(i\mathbf{q} \cdot \mathbf{R}_1) \\
\exp(i\mathbf{q} \cdot \mathbf{R}_2) \\
. \\
. \\
\exp(i\mathbf{q} \cdot \mathbf{R}_N)
\end{pmatrix}
\]  

(A18)

Here \( \mathbf{R}_j \) are the \( N = L^D \) lattice points of \( \mathbb{L}^{(D)}_L \) and \( \mathbf{e}_i \) are the basis vectors of \( \mathbb{R}^D \). The Bloch theorem provides exactly \( N \) independent \( \mathbf{q} \) vectors and thus \( N \) independent eigenvectors of \( Q(\mathbb{L}^{(D)}_L) \). It is this way that equations (16) were derived. This \( k \)-th power can be used to obtain the well known result in terms of multinomial coefficients for the number of directed walks on \( \mathbb{Z}^D \) between two points \( z = (z_1, z_2, \ldots, z_D) \) and \( s = (s_1, s_2, \ldots, s_D) \). In fact it suffices to calculate the element \( (z,s) \) of the matrix \( (Q(\mathbb{L}^{(D)}_L))^{\|z-s\|} \), with \( \| z - s \| = \sum_{i=1}^{D} \left| z_i - s_i \right| \), and \( L > 2 \| z - s \| \)

References