PHYSICAL REVIEW B, VOLUME 63, 064105

Coherent quasielastic neutron scattering: A theorem about total neutron scattering functions for rotational jump diffusion of molecules on a lattice

Gerrit Coddens
Laboratoire des Solides Irradiés, Ecole Polytechnique, F-91128-Palaiseau Cedex, France

(Received 16 June 2000; published 23 January 2001)

We derive a theorem about the *coherent* quasielastic neutron-scattering signal from a lattice of N molecules that are undergoing rotational jump diffusion. If no correlations between the molecular jumps exist then the coherent quasielastic scattering signal is just N times that of a single molecule. The elastic contribution is just the diffraction diagram of the system. This implies, among others, that between the Bragg peaks there is no coherent elastic contribution, i.e., between the Bragg peaks the coherent signal is purely quasielastic. These results for coherent scattering are in marked contrast to those in the case of incoherent scattering where one also can find elastic scattering outside the Bragg peaks.

DOI: 10.1103/PhysRevB.63.064105 PACS number(s): 61.12.Ex, 87.64.−t, 66.30.Dn

I. INTRODUCTION

Quasielastic neutron scattering[1,2] is a powerful tool to study relaxational motions within the realms of condensed matter physics, chemistry and biology. On consulting the few existing monographs[1,2] on this subject, the reader will soon notice that study cases and examples dealing with *incoherent* quasielastic neutron scattering abound, while applications within the domain of *coherent* scattering have remained very few and far between. In a concern to palliate this shortage of means in modeling, we have outlined in a series of previous papers[3] a method to calculate *total* neutron scattering functions $\mathcal{S}(\mathbf{Q},\omega)$, by reformulating the problem in terms of configurations. The whole system is represented by an abstract single particle that moves in a configuration space. Each site in this configuration space corresponds to one configuration of the system. The basic idea is the following. According to Van Hove,[4] the coherent and incoherent double-differential scattering cross sections are given by

$$\left[\frac{d^2\sigma}{d\Omega dE_f}\right]_{\text{inc}} = \frac{k_f}{k_i}\frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} e^{-\imath\omega t}\sum_j b_j^2 \langle e^{\imath\mathbf{Q}\cdot[\mathbf{r}_j(t)-\mathbf{r}_j(0)]}\rangle_{th}\,dt = \frac{k_f}{k_i}\frac{1}{2\pi\hbar}\mathcal{S}_{\text{inc}}(\mathbf{Q},\omega), \tag{1}$$

$$\left[\frac{d^2\sigma}{d\Omega dE_f}\right]_{coh} = \frac{k_f}{k_i}\frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} e^{-\imath\omega t}\sum_{j,k} b_j^* b_k \langle e^{\imath\mathbf{Q}\cdot[\mathbf{r}_k(t)-\mathbf{r}_j(0)]}\rangle_{th}\,dt = \frac{k_f}{k_i}\frac{1}{2\pi\hbar}\mathcal{S}(\mathbf{Q},\omega), \tag{2}$$

where we have introduced the incoherent and total scattering functions $\mathcal{S}_{inc}(\mathbf{Q},\omega)$ and $\mathcal{S}(\mathbf{Q},\omega)$. A comparison between the two equations reveals that in the case of incoherent scattering one must keep track of the history of one single particle (as manifested by the occurrence of a single index j), while in the case of coherent scattering one has to follow up the simultaneous evolution of all particles (as transpires through the occurrence of *two* indices j,k) within the system under investigation. The latter demand appears as a significant increase in theoretical complexity, which may be considered as the culprit of the aforementioned scantiness of literature on coherent quasielastic scattering. The term $\Sigma_{j,k} b_j^* b_k \langle\, e^{\imath\mathbf{Q}\cdot[\mathbf{r}_k(t)-\mathbf{r}_j(0)]}\rangle_{th}$ in Eq. (2) can be rewritten as

$$\left\langle \left(\sum_j b_j\, e^{\imath\mathbf{Q}\cdot\mathbf{r}_j(0)}\right)^* \left(\sum_k b_k\, e^{\imath\mathbf{Q}\cdot\mathbf{r}_k(t)}\right)\right\rangle_{th} = \langle[\mathcal{F}_{\mathcal{C}(0)}(\mathbf{Q})]^*[\mathcal{F}_{\mathcal{C}(t)}(\mathbf{Q})]\rangle_{th}, \tag{3}$$

where $\mathcal{F}_{\mathcal{C}(t)}(\mathbf{Q}) = \Sigma_k b_k\, e^{\imath\mathbf{Q}\cdot\mathbf{r}_k(t)}$ is the Fourier transform (weighted by the coherent scattering lengths of the nuclei) of the configuration $\mathcal{C}(t)$ of the atomic positions at time t. In the previous lines, the sums are over all the atoms in the system. The scattering lengths b_j, b_k to be plugged into the equations are the incoherent ones in Eq. (1) and the coherent ones in Eq. (2). The preceding lines already show that in order to describe a coherent scattering signal, it is much better to describe the system in terms of configurations. The terms $\Sigma_k b_k\, e^{\imath\mathbf{Q}\cdot\mathbf{r}_k(t)}$ are invariant under the exchange of two identical particles. Hence, coherent scattering does not distinguish individual particles and sees only configurations. Coherent scattering corresponds to the wave behavior of the neutron, while incoherent scattering, which does distinguish between individual particles, corresponds to the particle behavior of the neutron. This has been made intuitive by Feynman.[5]

It is our aim to illustrate the potential of our approach by applying it to a number of representative cases as a guide to our methodology that eventually should enable a general readership to acquire enough autonomy to put it to profit in his own possible systems of interest. The main point we want to make is that, although very often the size of the configuration space may look daunting, there do exist technical expedients to solve the problem in full generality that also an experimentalist should not find too difficult to master. In the present paper, we demonstrate the method by deriving a theorem about the total scattering function of a system of N rotating molecules, which we will be able to apply afterwards, e.g., to calculate the coherent neutron-scattering signal of the nonadecane molecules inside an urea inclusion compound,[6] a system that has received much current interest. The incentive for our calculation has been a request emanating from Toudic and his collaborators,[7] who have made an experimental study of the urea inclusion compound by coherent and incoherent quasielastic neutron scattering and NMR.[8] It is assumed that the lattice defined by the barycenters of the molecules is periodic and that *the molecules are rotating independently*. Their rotation axes and their orientations are all parallel (in the sense that when two molecules find themselves in an orientation that carries a label j, then they are strictly parallelly oriented) but the details of the rotational diffusion of the single molecules are, up to a certain extent, immaterial: it can be continuous or jump diffusion, and in the latter case the rotation axis may have arbitrary symmetry, e.g., $n\in\mathbb{N}$ (where we may add the convention $n=\infty$ for continuous diffusion, which is obtained from the case with finite n by taking the limit $n\rightarrow\infty$). The jump model with finite n is based on the usual assumptions in the white-noise approximation: (1) The duration of a jump is so short that it can be neglected; (2) jumps occur only between first-neighbor orientations and the time between two such $2\pi/n$ jumps follows an exponential distribution characterized by a so-called relaxation time τ; (3) due to the vanishing duration of a jump and the absence of any correlations, we can assume that two jumps never occur simultaneously. Calling the total number of molecules within the sample N, one's educated guess will then probably be that we can take N times the coherent signal of a single molecule in order to describe the full system. This intuitive idea has been put here on a firm footing by a rigorous mathematical proof based on the assumptions outlined above. Moreover, our approach also tells something about the elastic contribution. Furthermore, it indicates the path one will have to follow in order to tackle more involved situations where the molecular jumps no longer remain totally uncorrelated. The theorem derived says that the resulting signal contains two contributions, viz., an elastic one, which is nothing else than the (Bragg) diffraction diagram of the system, and a quasielastic one, which is just N times the coherent quasielastic scattering signal for a single rotating particle. This immediately implies that there is no elastic signal between the Bragg peaks as in the case for incoherent scattering, where it has become common practice to define an elastic incoherent structure factor (EISF) after Lechner's pioneering work.[9] The advantage of introducing this concept is that it allows one to get rid of the necessity to determine the Debye-Waller factor. If we want to render the analysis of the coherent quasielastic scattering signal insensitive to the Debye-Waller factor in a similar way, then we will have to compare the quasielastic intensities to those of the Bragg peaks. The importance of this finding for the studies of urea inclusion compounds is obvious. The coherent quasielastic signal for the rotational diffusion of a single alkane molecule can be calculated rigorously, for arbitrary values of n, such that a comparison with the experimental data will teach us unambiguously if the rotations of the nonadecane molecules are correlated or otherwise. Since there must exist some correlations if we are unable to reproduce the experimental results with some value of n. Surprisingly, the coherent data are compatible with a description based on the premise of total absence of correlations, while the incoherent data are not. A theoretical treatment of the coherent data allowing for some correlations will thus be required in the future. For one thing, the coherent neutron-scattering signals have indeed revealed themselves as being purely quasielastic in the regions in between the Bragg peaks. The circumstance that correlations do occur is beyond any possible doubt, the one an open-mind curiosity should be inclined to prefer, since it renders the subject matter actually much more rich and thrilling. In fact, the general method we developed can even then be put to use to calculate coherent signals in such systems, which leads to the unprecedented situation, where one would be able to gain access to a wealth of information about dynamical correlations between rotating molecules.

II. ROTATIONAL DIFFUSION OF A SINGLE MOLECULE

The rotational jumps for a single molecule μ around an n-fold axis are governed by n coupled rate equations:[1]

$$\frac{d}{dt}\mathbf{P}^{(\mu)}=\frac{1}{\tau}\mathbf{M}^{(\mu)}\mathbf{P}^{(\mu)}, \tag{4}$$

where the $n\times n$ jump matrix $\mathbf{M}^{(\mu)}$ is given by

$$\mathbf{M}^{(\mu)}=\begin{pmatrix} -2 & 1 & 0 & 0 & 0 & 0 & \cdots & 0 & 0 & 0 & 0 & 1\\ 1 & -2 & 1 & 0 & 0 & 0 & \cdots & 0 & 0 & 0 & 0 & 0\\ 0 & 1 & -2 & 1 & 0 & 0 & \cdots & 0 & 0 & 0 & 0 & 0\\ 0 & 0 & 1 & -2 & 1 & 0 & \cdots & 0 & 0 & 0 & 0 & 0\\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & & \vdots & \vdots & \vdots & \vdots & \vdots\\ 0 & 0 & 0 & 0 & 0 & 0 & \cdots & 1 & -2 & 1 & 0 & 0\\ 0 & 0 & 0 & 0 & 0 & 0 & \cdots & 0 & 1 & -2 & 1 & 0\\ 0 & 0 & 0 & 0 & 0 & 0 & \cdots & 0 & 0 & 1 & -2 & 1\\ 1 & 0 & 0 & 0 & 0 & 0 & \cdots & 0 & 0 & 0 & 1 & -2 \end{pmatrix} \tag{5}$$

and τ is the relaxation time for a nearest-neighbor jump (i.e., over an angle $2\pi/n$). The $n\times 1$ column matrix $\mathbf{P}^{(\mu)} = [\,p_1^{(\mu)}(t), p_2^{(\mu)}(t), \cdots, p_j(t), \cdots, p_n^{(\mu)}(t)\,]^\top$ contains the probabilities $p_j^{(\mu)}(t)$ that the molecule with label μ has the orientation $j\in[1,n]\cap\mathbb{N}$ at time t. The rate Eqs. (4) and (5) can be rewritten as

$$\frac{d}{dt}p_j^{(\mu)} = \frac{1}{\tau}[\,p_{j-1}^{(\mu)} - 2p_j^{(\mu)} + p_{j+1}^{(\mu)}\,], \tag{6}$$

where all lower indices have be taken *modulo n*. Each orientation or configuration j has the same type of relation with its nearest neighbors $j-1$ and $j+1$, such that our problem has translational invariance. It is impossible to tell from the structure of the relation at a given orientation which particular value j takes, as the structure is identical for all j. This has been pointed out previously[3] by drawing the attention of the reader to the fact that the matrix $\mathbf{M}^{(\mu)}$ is the same as the one that occurs in the phonon problem of a monoatomic periodic linear chain of n atoms with cyclic boundary conditions, provided one makes allowance for the fact that $1/\tau$ must be replaced by κ/m, where κ is the force constant and m the mass of the atom. (Of course the system of coupled differential equations is of the second order in the phonon problem, but in any case, the mathematical solution of the equations also here boils down to the diagonalization of the matrix $\mathbf{M}$.) In the phonon problem the eigenvectors $\mathbf{V}^{(q)}$ are immediately given by the Bloch ansatz $(\mathbf{V}^{(q)})_j = \exp[\imath\,(2\pi/n)\,(q-1)\,(j-1)]$ which is a mere offshoot of the underlying translational invariance. The corresponding eigenvalues λ_q are obtained by operating $\mathbf{M}^{(\mu)}$ on $\mathbf{V}^{(q)}$:

$$\lambda_q = -4\sin^2\left[\frac{\pi}{n}(q-1)\right] \quad \forall q\in[1,n]\cap\mathbb{N}. \tag{7}$$

III. FORMULATION OF THE PROBLEM WITH TWO MOLECULES

If two molecules μ and ν are rotating independently, then the joint probability $\mathcal{P}_{j;\,k}$ that molecule μ has orientation j and molecule ν has orientation k will be given by $\mathcal{P}_{j;\,k} = p_j^{(\mu)}\,p_k^{(\nu)}$. By combining

$$[\times\, p_k^{(\nu)}]: \tau\frac{d}{dt}p_j^{(\mu)} = p_{j-1}^{(\mu)} - 2\,p_j^{(\mu)} + p_{j+1}^{(\mu)} \qquad \forall j\in\{1,2,\ldots,n\}, \tag{8}$$

$$[\times\, p_j^{(\mu)}]: \tau\frac{d}{dt}p_k^{(\nu)} = p_{k-1}^{(\nu)} - 2\,p_k^{(\nu)} + p_{k+1}^{(\nu)} \qquad \forall k\in\{1,2,\ldots,n\}$$

we obtain exactly

$$\tau\frac{d}{dt}\mathcal{P}_{j;\,k} = \mathcal{P}_{j-1;\,k} + \mathcal{P}_{j+1;\,k} + \mathcal{P}_{j;\,k-1} + \mathcal{P}_{j;\,k+1} - 4\,\mathcal{P}_{j;\,k} \qquad \forall (j,k)\in\{1,2,\ldots,n\}^2. \tag{9}$$

If in the analogon of the phonon problem we go from the problem of a linear chain to a two-dimensional lattice, we know that instead of eigenvectors $\mathbf{V}^{(q)}$ with components $(\mathbf{V}^{(q)})_j = \exp[\imath(2\pi/n)\,(q-1)\,(j-1)]$ we will have to take Bloch waves of the type $(\mathbf{V}^{(q_x\,;\,q_y)})$ where $(\mathbf{V}^{(q_x\,;\,q_y)})_{j_x\,;\,j_y} = \exp\{\,2\pi\imath[(q_x-1)\,(j_x-1)+(q_y-1)\,(j_y-1)]\}$. The eigenvectors $(\mathbf{V}^{(q_x\,;\,q_y)})$ are given two indices [corresponding to a two-dimensional wave vector $(q_x\,;q_y)$], since there will now be $n\times n$ of them (there are $n\times n$ atoms on a square lattice of linear dimensions $n\times n$). The dynamical matrix for the phonon problem has then also $n\times n$ lines, which is why we also use double indices (j_x, j_y). The order of enumeration of the latter indices inside an eigenvector of the dynamical matrix $(\mathbf{V}^{(q_x;q_y)})$ is not important, provided one takes care to stick to the same convention throughout. This indicates that the eigenvectors and eigenvalues for a two-dimensional case can be constructed from those of the one-dimensional case by making products. The product that comes into play is the so-called Kronecker product of matrices. The eigenvectors will be

$$\mathbf{V}^{(q_x\,;\,q_y)} = \mathbf{V}^{(q_x)}\otimes\mathbf{V}^{(q_y)} \tag{10}$$

and the corresponding eigenvalues will be

$$\lambda_{q_x\,;\,q_y} = \lambda_{q_x} + \lambda_{q_y} = -4\sin^2\left[\frac{\pi}{n}(q_x-1)\right] - 4\sin^2\left[\frac{\pi}{n}(q_y-1)\right]. \tag{11}$$

Equation (9) is now exactly the same as the one for the jump diffusion of a single particle on a two-dimensional lattice of $n\times n$ sites and cyclic boundary conditions, the site with indices (j,k) having four neighbors $(j-1,k)$, $(j+1,k)$, $(j,k-1)$, and $(j,k+1)$. In fact, it has two neighbors $(j-1,k)$ and $(j+1,k)$ along the x direction and two neighbors $(j,k-1)$ and $(j,k+1)$ along the y direction. The configuration space is thus the Cartesian product of the configuration spaces of the two molecules. These heuristic arguments are purely mathematical and one should not try to give them a physical interpretation. By noticing a formal analogy between our jump problem and the problem of phonons on a two-dimensional lattice, we are able to find the eigenvectors of the jump matrix defined in Eq. (9), but the translational symmetry we exploit in configuration space has nothing to do with any periodicity in the physical space that harbors the two molecules.

IV. GENERAL FORMULATION FOR *N* MOLECULES

This can be generalized to an arbitrary number N of independently rotating molecules $\mu_1, \mu_2, \ldots, \mu_l, \ldots, \mu_{N-1}, \mu_N$. We end up with the jump diffusion of a single abstract particle (our configuration) on a hypercubic lattice of dimension N (our configuration space), due to the rule for the derivative of a product. Here each site will have $2N$ neighbors, viz., two along each coordinate axis x_{ℓ} of the hypercubic lattice in $\mathbb{R}^N$. In N dimensions we will have probabilities

$$\mathcal{P}_{j_1;\,j_2;\,\cdots j_l;\cdots\, j_{N-1};\,j_N} = p^{(\mu_1)}_{j_1}\, p^{(\mu_2)}_{j_2} \cdots p^{(\mu_l)}_{j_l} \cdots p^{(\mu_{N-1})}_{j_{N-1}}\, p^{(\mu_N)}_{j_N} \qquad \forall (j_1,j_2,\cdots j_{N-1},j_N)\in\{1,2,\cdots,n\}^N. \tag{12}$$

The eigenvectors will be

$$\mathbf{V}^{(q_1\,q_2\,\cdots\,q_l\,\cdots\,q_{N-1}\,q_N)} = \mathbf{V}^{(q_1)}\otimes\mathbf{V}^{(q_2)}\otimes\cdots\otimes\mathbf{V}^{(q_l)}\otimes\cdots\otimes\mathbf{V}^{(q_{N-1})}\otimes\mathbf{V}^{(q_N)}, \tag{13}$$

$\forall (q_1,q_2,\ldots,q_l,\ldots,q_{N-1},q_N)\in\{1,2,\ldots,n\}^N$ and the corresponding eigenvalues will be

$$\lambda_{q_1;\,q_2;\,\ldots;\,q_l;\,\ldots;\,q_{N-1};\,q_N} = \lambda_{q_1}+\lambda_{q_2}+\cdots\lambda_{q_l}+\cdots+\lambda_{q_{N-1}}+\lambda_{q_N}, \tag{14}$$

where, more explicitly, the right hand side reads

$$-4\sin^2\left[\frac{\pi}{n}(q_1-1)\right]-4\sin^2\left[\frac{\pi}{n}(q_2-1)\right]\cdots -4\sin^2\left[\frac{\pi}{n}(q_l-1)\right]\cdots-4\sin^2\left[\frac{\pi}{n}(q_{N-1}-1)\right] -4\sin^2\left[\frac{\pi}{n}(q_N-1)\right]. \tag{15}$$

In such a problem, a site with coordinates $(j_1,j_2,\ldots j_{N-1},j_N)$ within the interior of the set $\{1,2,\ldots,n\}^N$ will have $2N$ neighbors. This will also be true for the points on the boundary of this set due to the cyclic boundary conditions, and the corresponding jump matrix $\mathbf{M}$ (where we have labeled the molecules μ_l canonically by $l\in[1,N]\cap\mathbb{N}$) will then have $2N+1$ nonzero entries on each line and in each column, $2N$ with the value 1 and one with the value $-2N$. In more condensed form we can write the probabilities as $\mathcal{P}_{\mathbf{j}}$, with $\mathbf{j}\in([1,n]\cap\mathbb{N})^N$. The n^N eigenvectors are then

$$\mathbf{V}^{(\mathbf{q})} = \otimes_{l=1}^{N}\mathbf{V}^{(q_l)}, \tag{16}$$

with $\mathbf{q}\in([1,n]\cap\mathbb{N})^N$. This means that these n^N eigenvectors are $n^N\times 1$ column matrices, whose elements are defined by

$$(\mathbf{V}^{(\mathbf{q})})_{\mathbf{j}} = \frac{1}{\sqrt{n^N}}\prod_{l=1}^{N}\exp\left[\imath\frac{2\pi}{n}(j_l-1)(q_l-1)\right] = \frac{1}{\sqrt{n^N}}\exp\left[\imath\frac{2\pi}{n}\sum_{l=1}^{N}(q_l-1)(j_l-1)\right]. \tag{17}$$

This equation illustrates the meaning of the matrix Kronecker product $\otimes$ that we used in the preceding lines. The term $1/\sqrt{n^N}$ is the normalization factor for the eigenvector. The corresponding eigenvalues are

$$\lambda_{\mathbf{q}} = \sum_{l=1}^{N} -4\sin^2\left[\frac{\pi}{n}(q_l-1)\right]. \tag{18}$$

The jump matrix $\mathbf{M}$ is a $n^N\times n^N$ matrix.

V. CALCULATION OF THE TOTAL SCATTERING FUNCTION

The jump model can be solved by using $\mathbf{M}=\mathbf{S}\,\boldsymbol{\Lambda}\,\mathbf{S}^{-1}$ where $\boldsymbol{\Lambda}$ is a diagonal matrix whose elements are the eigenvalues given in Eq. (18) and $\mathbf{S}$ is obtained by juxtaposition of the eigenvectors given in Eqs. (16) and (17), within the same order as their corresponding eigenvalues on the diagonal of $\boldsymbol{\Lambda}$. It can be shown that $\mathbf{S}^{-1}=\mathbf{S}^{\dagger}$, such that the solution of

$$\frac{d}{dt}\mathbf{P} = \frac{1}{\tau}\mathbf{M}\,\mathbf{P} \tag{19}$$

becomes

$$\mathbf{P}(t) = \mathbf{S}\,e^{\boldsymbol{\Lambda}t/\tau}\;\mathbf{S}^{\dagger}\mathbf{P}(0), \tag{20}$$

where the $n^N\times 1$ column matrix $\mathbf{P}(0)$ contains the initial conditions. When we calculate thermal averages, we have to consider all possible initial conditions and average over them according to their relative probabilities (i.e., thermal occupation factors). The initial condition $\mathbf{P}(0)$ just tells us in which configuration the system was at time 0. That could have been configuration 1, configuration 2, etc., up to configuration n^N. These initial configurations are represented by the n^N column matrices $[1,0,0,\ldots,0,0]^{\top}$, $[0,1,0,\ldots,0,0]^{\top}$, $\ldots$,$[0,0,0,\ldots,1,0]^{\top}$, $[0,0,0,\ldots,0,1]^{\top}$, The configuration $\mathbf{j}$ has all its entries zero, except on the line that corresponds to the index $\mathbf{j}$, where the matrix contains a 1. In principle, we can give all these configurations the same equal weight, $1/n^N$. Each initial configuration $\mathbf{j}$ will correspond then to a $n^N\times 1$ column vector that contains zeroes on all lines, except on line $\mathbf{j}$ where it will contain $1/n^N$. The juxtaposition of these n^N column vectors of initial conditions will yield then $\mathbb{I}/n^N$ such that

$$\mathcal{S}(\mathbf{Q},\omega) = \frac{1}{n^N}\mathbf{F}\,\mathbf{S}\;\;\mathcal{F}(\,e^{\boldsymbol{\Lambda}t/\tau})\;\mathbf{S}^{\dagger}\,\mathbb{I}\,\mathbf{F}^{\dagger}, \tag{21}$$

where $\mathbf{F}$ is the $1\times n^N$ row matrix that contains the spatial Fourier transforms $F_{\mathbf{j}}$ of the configurations $\mathbf{j}$ obtained by putting a Dirac measure of weight b_x at the position of each atom of type x [b_x is its coherent scattering length (see Sec. I)]:

$$F_{\mathbf{j}} = \mathcal{F}_{j_1}\,e^{\imath\mathbf{Q}\cdot\mathbf{r}_1}+\mathcal{F}_{j_2}\,e^{\imath\mathbf{Q}\cdot\mathbf{r}_2}+\cdots+\mathcal{F}_{j_l}\,e^{\imath\mathbf{Q}\cdot\mathbf{r}_l}+\cdots+\mathcal{F}_{j_{N-1}}\,e^{\imath\mathbf{Q}\cdot\mathbf{r}_{N-1}}+\mathcal{F}_{j_N}\,e^{\imath\mathbf{Q}\cdot\mathbf{r}_N} = \sum_{l=1}^{N}\mathcal{F}_{j_l}\,e^{\imath\mathbf{Q}\cdot\mathbf{r}_l}. \tag{22}$$

Here $\mathcal{F}_{j_l}$ is this Fourier transform (weighted by the appropriate coherent scattering lengths) of molecule l if it were placed at the origin, in one of its n possible orientations j_l, while $\mathbf{r}_l$ is the position vector of its center of gravity. Hence, when we enumerate the configurations $\mathbf{j}$ in lexicographical order,

$$\mathbf{F}=[F_{(1,1,\ldots,1)},F_{(1,1,\ldots,2)},\ldots,F_{(1,1,\ldots,n)},\ldots,F_{(n,n,\ldots,n)}]. \tag{23}$$

Writing the temporal Fourier transform $\mathcal{F}(e^{\boldsymbol{\Lambda}t/\tau})=\mathbf{L}(\omega)$, we obtain

$$\mathcal{S}(\mathbf{Q},\omega)=\frac{1}{n^N}\,\mathbf{F}\,\mathbf{S}\,\mathbf{L}(\omega)\,\mathbf{S}^\dagger\,\mathbf{F}^\dagger. \tag{24}$$

The elements of the diagonal matrix $\mathbf{L}(\omega)$ are Dirac measures $\delta(\omega)$, when the eigenvalue $\lambda_{\mathbf{q}}$ is zero. In the other cases they are Lorentzians $L(\hbar\lambda_{\mathbf{q}}/\tau,\omega)$ of width $\hbar\lambda_{\mathbf{q}}/\tau$. (Here $L(\hbar\Gamma,\omega)=(1/\pi)[\Gamma/(\Gamma^2+\omega^2)]$). It will be convenient to split the term $1/n^N$ over the left- and right-hand side of Eq. (24) and introduce the definition of the $n^N\times 1$ matrix $\mathbf{G}$:

$$\mathbf{G}=\frac{1}{\sqrt{n^N}}\mathbf{F}\,\mathbf{S}, \tag{25}$$

which leads to

$$\mathcal{S}(\mathbf{Q},\omega)=\mathbf{G}\,\mathbf{L}(\omega)\,\mathbf{G}^\dagger \tag{26}$$

and

$$G_{\mathbf{q}}=\frac{1}{\sqrt{n^N}}\sum_{\mathbf{j}}\;F_{\mathbf{j}}\,S_{\mathbf{j}\,;\,\mathbf{q}}, \tag{27}$$

which more explicitly reads as

$$G_{\mathbf{q}}=\frac{1}{\sqrt{n^N}}\sum_{j_1=1}^{n}\sum_{j_2=1}^{n}\cdots\sum_{j_l=1}^{n}\cdots\sum_{j_{N-1}=1}^{n}\sum_{j_N=1}^{n}F_{j_1;\,j_2;\,\ldots j_l;\,\ldots j_{N-1};\,j_N}\,S_{j_1;\,j_2;\,\ldots j_l;\,\ldots j_{N-1};\,j_N;\,q_1;\,q_2;\,\ldots q_k;\,\ldots q_{N-1};\,q_N}. \tag{28}$$

Here $F_{j_1;\,j_2;\,\ldots j_l;\,\ldots j_{N-1};\,j_N}$ is given by Eq. (22), while $S_{j_1;\,j_2;\,\ldots j_l;\,\ldots j_{N-1};\,j_N;\,q_1;\,q_2;\,\ldots q_k;\,\ldots q_{N-1};\,q_N}$ is given by Eq. (17):

$$G_{q_1;\,q_2;\,\cdots q_k;\,\cdots q_{N-1};\,q_N}=\frac{1}{n^N}\sum_{j_1=1}^{n}\sum_{j_2=1}^{n}\cdots\sum_{j_l=1}^{n}\cdots\sum_{j_{N-1}=1}^{n}\sum_{j_N=1}^{n}\left[\sum_{v=1}^{N}\;\mathcal{F}_{j_v}\,e^{\imath\mathbf{Q}\cdot\mathbf{r}_v}\right]\left[\prod_{k=1}^{N}\;e^{\imath(2\pi/n)\,(j_k-1)\,(q_k-1)}\right]. \tag{29}$$

We will first of all perform the sum over v. The general term in this sum can be decomposed as

$$\frac{1}{n^N}\left[\sum_{j_v}\;\mathcal{F}_{j_v}\,e^{\imath(2\pi/n)\,(j_v-1)\,(q_v-1)}\,e^{\imath\mathbf{Q}\cdot\mathbf{r}_v}\right]\left[\sum_{j_1=1}^{n}\sum_{j_2=1}^{n}\cdots\sum_{j_{v-1}=1}^{n}\sum_{j_{v+1}=1}^{n}\cdots\sum_{j_{N-1}=1}^{n}\sum_{j_N=1}^{n}\prod_{k\neq v}\;e^{\imath(2\pi/n)\,(j_k-1)\,(q_k-1)}\right], \tag{30}$$

where the term between the second pair of brackets can be factorized as

$$\prod_{k\neq v}\left[\sum_{j_k=1}^{n}\;e^{\imath(2\pi/n)\,(j_k-1)\,(q_k-1)}\right]. \tag{31}$$

Only the term in v is missing here. Each term of this product has the same mathematical structure. If $q_k=1$, all exponentials in the sum over j_k become equal to 1. As there are n of them, we get n for the sum, while

$$\forall q_k\neq 1{:}\sum_{j_k=1}^{n}\;e^{\imath(2\pi/n)(j_k-1)(q_k-1)}=\frac{e^{\imath 2\pi(q_k-1)}-1}{e^{\imath(2\pi/n)(q_k-1)}-1}=0. \tag{32}$$

Indeed, when $q_k\neq 1$, the denominator is not zero, while the numerator is. Hence Eq. (31) is seen to yield

$$n^{N-1}\,\delta_{q_1;\,1}\,\delta_{q_2;\,1}\cdots\,\delta_{q_{v-1};\,1}\,\delta_{q_{v+1};\,1}\cdots\,\delta_{q_{N-1};\,1}\,\delta_{q_N;\,1}. \tag{33}$$

Thus we obtain

$$\begin{aligned}G_{q_1;\,q_2;\,\ldots q_k;\,\ldots q_{N-1};\,q_N}&=\frac{1}{n}\sum_{v=1}^{N}\sum_{j_v=1}^{n}\;\mathcal{F}_{j_v}\,e^{\imath(2\pi/n)\,(j_v-1)\,(q_v-1)}\,e^{\imath\mathbf{Q}\cdot\mathbf{r}_v}\\&\quad\times\delta_{q_1;\,1}\,\delta_{q_2;\,1}\cdots\,\delta_{q_{v-1};\,1}\,\delta_{q_{v+1};\,1}\cdots\,\delta_{q_{N-1};1}\,\delta_{q_N;\,1}.\end{aligned} \tag{34}$$

As Eq. (26) shows, the Lorentzian $L(\hbar\lambda_{\mathbf{q}}/\tau,\omega)$ will be associated with $|G_{\mathbf{q}}|^2$, such that the normalization prefactor becomes n^{-2} , which is independent of N and already foreshadows the fact that in the end we will have n^2 different Lorentzians. $|G_{\mathbf{q}}|^2$ will give rise to N terms of the type ($v=w$):

$$\frac{1}{n^2}\left|\sum_{j_v=1}^{n}\mathcal{F}_{j_v}\,e^{\imath(2\pi/n)(j_v-1)(q_v-1)}e^{\imath\mathbf{Q}\cdot\mathbf{r}_v}\right|^2\delta_{q_1;1}\;\delta_{q_2;1}\cdots\delta_{q_{v-1};1}\,\delta_{q_{v+1};1}\cdots\delta_{q_{N-1};1}\,\delta_{q_N;1}, \tag{35}$$

and $N(N-1)$ cross products of the type ($v\neq w$)

$$\begin{aligned}&\frac{1}{n^2}\sum_{j_w=1}^{n}\mathcal{F}_{j_w}\,e^{\imath(2\pi/n)(j_w-1)(q_w-1)}e^{\imath\mathbf{Q}\cdot\mathbf{r}_w}\,\delta_{q_1;1}\,\delta_{q_2;1}\cdots\delta_{q_{w-1};1}\,\delta_{q_{w+1};1}\cdots\delta_{q_{N-1};1}\,\delta_{q_N;1}\\&\times\sum_{j_v=1}^{n}\mathcal{F}^{*}_{j_v}\,e^{-\imath(2\pi/n)(j_v-1)(q_v-1)}e^{-\imath\mathbf{Q}\cdot\mathbf{r}_v}\,\delta_{q_1;1}\,\delta_{q_2;1}\cdots\delta_{q_{v-1};1}\,\delta_{q_{v+1};1}\cdots\delta_{q_{N-1};1}\,\delta_{q_N;1}.\end{aligned} \tag{36}$$

In the latter expression every term $\delta_{q_l;1}$ occurs at least once $\forall l\in[1,n]\cap\mathbb{N}$, since $v\neq w$. As such it yields

$$\begin{aligned}&\frac{1}{n^2}\sum_{j_w=1}^{n}\mathcal{F}_{j_w}e^{\imath\mathbf{Q}\cdot\mathbf{r}_w}\sum_{j_v=1}^{n}\mathcal{F}^{*}_{j_v}e^{-\imath\mathbf{Q}\cdot\mathbf{r}_v}\,\delta_{\mathbf{q};(1,1,\cdots,1)}\\&=\frac{1}{n^2}\left|\sum_{j_w=1}^{n}\mathcal{F}_{j_w}\right|^2\frac{1}{n^2}e^{\imath\mathbf{Q}\cdot(\mathbf{r}_w-\mathbf{r}_v)}\,\delta_{\mathbf{q};(1,1,\cdots,1)}.\end{aligned} \tag{37}$$

Since we suppose that all molecules explore the same set of n different orientations, we can rewrite

$$\left|\sum_{j_w=1}^{n}\mathcal{F}_{j_w}\right|^2=\left|\sum_{j=1}^{n}\mathcal{F}_{j}\right|^2. \tag{38}$$

There are now two cases to be distinguished:

$$\begin{aligned}&(\forall\;\; w\in[1,n]\cap\mathbb{N})\;q_w=1,\\&(\exists!\,w\in[1,n]\cap\mathbb{N})\;q_w\neq1.\end{aligned} \tag{39}$$

The first case collects N contributions from Eq. (35) and $N(N-1)$ contributions of the type Eq. (38), which sum up to

$$\frac{1}{n^2}\left|\sum_{j=1}^{n}\mathcal{F}_j\right|^2\left|\sum_{w=1}^{N}e^{\imath\mathbf{Q}\cdot\mathbf{r}_w}\right|^2=\frac{1}{n^2}\left|\sum_{j=1}^{n}\mathcal{F}_j\right|^2\times\mathcal{S}(\mathbf{Q})_{lattice}, \tag{40}$$

which becomes a prefactor of $\delta(\omega)$. Here $(1/n^2)\,|\Sigma_{j=1}^{n}\mathcal{F}_j|^2$ can be considered as an averaged form factor of the molecule, while $\mathcal{S}(\mathbf{Q})_{lattice}$ is the diffraction diagram of the (Bravais) lattice defined by the molecular positions. This shows that the elastic term is nothing else than the diffraction diagram of the sample (if we do not consider the host lattice). It also implies that there is no elastic intensity except the Bragg peaks that stands in marked contrast to the situation normally encountered in the case of incoherent scattering. In the second case, the notation $\exists!w$ means that there exists a unique w. This implies that only $n-1$ eigenvalues $-4\sin^2[(\pi/n)(q-1)];q=2,3,\ldots n-1,n$ have a nonzero form factor. In other words, in Eq. (14) all λ_{q_l} except one must be zero. The same nonzero eigenvalue can occur at position $l=1$, $l=2,\ldots,l=N$ in the sum, such that the same final result $-4\sin^2[(\pi/n)(q-1)]$ can be obtained in N distinct ways. Therefore, the form factor of the Lorentzian $L(\hbar\lambda_q/\tau,\omega)$ will be

$$\frac{N}{n^2}\left|\sum_{j=1}^{n}\mathcal{F}_j\,e^{\imath(2\pi/n)(j-1)(q-1)}\right|^2, \tag{41}$$

which is nothing else than N times the form factor of the same Lorentzian in the coherent quasielastic neutron scattering from a single isolated molecule. This ends the proof of our theorem

$$\begin{aligned}\mathcal{S}(\mathbf{Q},\omega)=\delta(\omega)\times\frac{1}{n^2}\left|\sum_{j=1}^{n}\mathcal{F}_j\right|^2\mathcal{S}(\mathbf{Q})_{lattice}\\+\sum_{q=2}^{n}L\left[\frac{4\hbar}{\tau}\sin^2\left(\frac{\pi}{n}(q-1)\right),\omega\right]\\\times\frac{N}{n^2}\left|\sum_{j=1}^{n}\mathcal{F}_j\,e^{\imath(2\pi/n)(j-1)(q-1)}\right|^2.\end{aligned} \tag{42}$$

VI. FINAL CONCLUSIONS

It may be noted that our derivation remains valid if the lattice of molecular positions is not periodic, although we do not have a real-world application of this particular possibility in mind, especially since we have assumed that all molecular orientations are parallel. Nevertheless, this remark is instrumental to elucidate that the essential feature that enables us to fall back onto the Bloch ansatz in $\mathbb{R}^N$ is not the periodicity of the physical lattice in $\mathbb{R}^3$, but the cyclic character of the configuration space for the rotational motion of a single molecule. The gist of our method, crystallized within Eqs. (12–

14), is also of sufficient generality to accomodate other situations, e.g., rotational diffusion in fullerenes.[7] The point is that in the absence of correlations, the eigenvectors for the secular matrix that describe the simultaneous time evolution of several particles are just Kronecker products of the eigenvectors that one comes across in the rate equations for a single particle. The eigenvalues of the many-particle problem are sums of those for the single-particle problem. Hence, if one knows to diagonalize the relevant matrix in the single-particle problem, then one should in principle be apt to do it also for the many-particle problem, even if at first sight this might look as a real feat of ingenuity. It might be worth making the reader aware of the fact that we even do not have to bother about writing down the secular matrix explicitly, since one can move on to the determination of the really useful objects, which are its eigenvectors and eigenvalues, immediately. It is one of those aesthetic joys of mathematics that one can diagonalize huge matrices (of arbitrary size) in one's head even without ever considering to write them down onto paper. Skipping this step represents an important economy of efforts in problems with many particles. The configuration space of the many-particle problem is a Cartesian product of configuration spaces of the single-particle problems. Actually the product at stake is more than just a Cartesian product, since it also involves the connectivities of the configuration spaces. We do not know the well-defined mathematical terminology for such a product. In future contributions we will also try to make contact with situations where there do exist correlations between molecular motions on a lattice. Correlations tend to spoil the initial simplicity of a game considerably. We have already touched upon correlations in Ref. 3, and it can be seen from the example treated there (taken from the field of quasicrystals) that the strategy based on the use of a Kronecker product will in general be at a loss in situations where correlations come into play. Further illustrations of our method will also follow in other domains: the rotational jump diffusion of a CH_3D or a CD_3H molecule, and the translational jump diffusion of n identical particles on a periodic d-dimensional ($d \leqslant 3$) lattice of N^d sites (with $N^d > n$). In the latter case, the ''fermionic'' condition that two particles cannot share the same site severely complicates the solution of a problem that otherwise would have been straightforward.

---

[1] M. Bée, *Quasielastic Neutron Scattering* (Hilger, Bristol, 1988).

[2] T. Springer, *Quasielastic Neutron Scattering*, Springer Tracts in Physics Vol. 64 (Springer Verlag, Berlin, 1972).

[3] G. Coddens, J. Phys. I **4**, 921 (1994); G. Coddens and S. Lyonnard, Physica B **226**, 28 (1996); **233**, 93 (1997); G. Coddens, J. Phys. IV **10**, 151 (2000).

[4] L. Van Hove, Phys. Rev. **95**, 249 (1954).

[5] R. P. Feynman, in *The Feynman Lectures of Physics*, Quantum Mechanics, edited by R. P. Feynman, R. B. Leighton, and M. Sands (Addison-Wesley, Reading, MA, 1963).

[6] R. Lefort, J. Etrillard, B. Toudic, F. Guillaume, T. Breczewski, and P. Bourges, Phys. Rev. Lett. **77**, 4027 (1996).

[7] B. Toudic (private communication).

[8] H. Le Lann, Ph.D. thesis, University of Rennes 1, 2000.

[9] R. E. Lechner, in *Proceedings of the Conference on Neutron Scattering, Gatlinburg, June 1976*, edited by R. M. Moon (National Technical Information Service, U.S. Department of Commerce, Springfield, 1976), Vol. 1, p. 310.