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# Coherent quasielastic neutron scattering and correlations between rotational jumps of molecules on a periodic lattice

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**Abstract.** We previously [Coddens, Phys. Rev. **63**, 064105 (2001)] derived a theorem about the *coherent* quasielastic neutron-scattering signal from a $d$-dimensional lattice of $N$ molecules that are undergoing rotational jump diffusion (around an $n$-fold axis), assuming that there are no correlations between the molecules. In the present paper molecular correlations are treated, but only in the sense that several molecules could reorient simultaneously as in a cog-wheel mechanism. Moreover, we do not examine the possibility that the relaxation times of these combined reorientations could depend on details of the local environment created by the neighbouring molecules. Finally also an ergodicity condition has to be fulfilled. Admitting for all these assumptions we can show that the correlations do not affect the coherent quasielastic scattering pattern in the following sense: The functions of $Q$ that intervene in the description of the intensities remain unaltered, while the functions of $\omega$ can undergo a renormalization of the time scales. The latter changes cannot be detected as the time scales that would occur if the dynamics were independent are not available for comparison. In other words: Coherent quasielastic neutron scattering is not able to betray the existence of correlations of the restricted type that occur in our model. The assumptions that underly the model we present were made to allow a mathematically rigorous calculation of the scattering function. Other, perhaps more realistic cases may entail correlations of a type that is too difficult to be treated rigorously with our method of calculation. But our result presents an important non-trivial counterexample to show that the absence of a clue for the presence of correlations in the data is not a sufficient criterium to conclude that such correlations are indeed absent.

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## 1 Introduction

In a recent paper [1] we calculated the coherent quasielastic neutron-scattering signal [2–4] that results from $n$-fold rotational jumps of $N$ molecules periodically arranged on the sites of a $d$-dimensional solid-state lattice, by applying a previously described method [5]. *The jumping molecules themselves do not need to have n-fold symmetry.* As a physical visualization of the present problem we could mention the array of nonadecane molecules hosted by an urea inclusion compound [6]. (Such molecules have $CH_3$ end groups of three-fold symmetry, but the entire molecule has no such symmetry.)

In a first approach, we assumed that the molecules are jumping independently, leaving open the question: What could happen if the relaxational motions of neighbouring molecules cease to be uncorrelated? We anticipated that in that case coherent quasielastic neutron scattering might be able to evidence possible correlations. In the present paper we address this possibility, understanding the word correlation in the sense that within connected sets of a given size and shape all molecules jump simultaneously in some phase or anti-phase relations, like in a cog-wheel mechanism. In the paper we will use the word “clusters” to refer to these sets. Assuming further that the relaxation times for these combined jumps do not depend on the momentaneous orientations of the molecules inside (and outside) the cluster, we come to the astounding (and disappointing) conclusion that such correlations do not leave a fingerprint in the structure factors of the ensuing coherent dynamical signal. (See the abstract or below for a more precise formulation of the restrictions.) In other words: It is impossible to decide if such correlations are present and to determine their nature on the mere basis of the corresponding coherent quasielastic neutron scattering data.

Let us point out where the surprise lies. Quite often, if we calculate the total structure factor for such dynamics within a single isolated cluster, we will be able to

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detect the presence of such correlations, as we do not find the same answer as for the jump dynamics of a single molecule. Even when the cluster is not isolated, highly correlated rotors still can be expected to manifest themselves very differently in reciprocal space than independent rotors, *e.g.* in a linear chain anticorrelated *configurations* produced by the dynamics would manifest themselves at the $Q$-value corresponding to the zone boundary of the reciprocal lattice. Indeed, the correlated dynamics can give rise to static correlations between the orientations of the molecules, that should be observable. How is our result then possible? This question resumes one of the counterintuitive aspects of our result.

The crucial point is that the clusters we consider can be centered on any point of the crystal lattice, such that two clusters situated on neighbouring points can overlap. If the cog-wheels of two such points have ground in succession then the rotations involved in the second move will partly undo the static correlations that existed between the molecules after the first move. In such kind of dynamics the correlations are no longer as all-out that we can call them “ferro” or “anti-ferro” (as in the example of anti-correlated configurations above). To complicate things further, they are not necessarily zero either. They can be of an intermediate strength. How the story goes further, really will depend on the specific dynamics defined within the cog-wheel mechanism. *E.g.* it is conceivable that in certain dynamical models the memory of the initial static correlations in a single cluster (or in the crystal), eventually are totally washed out with time, due to the actions from overlapping clusters. We then have a different situation than the one evoked for a problem of an isolated cluster where the static correlations might persist indefinitely. Equally conceivable are other models, where such a total loss of memory does not occur.

We will distinguish two mutually exclusive possibilities: (1) The loss of memory with time is total, such that starting from any initial configuration that one could obtain by independent dynamics we can move to any other configuration that could be obtained by independent dynamics. We will call this the ergodic case. (2) On the contrary, in the non-ergodic case not all configurations can be reached. The configuration space that applied for the independent dynamics then splits up in several disjoint subsets. Only one of these is the set of possible states of the sample under study. All other states just do not exist in the sample.

Neutron scattering calculations involve an average over all possible initial states. In the ergodic case, this averaging will run over the same set of initial states as in the case of independent dynamics. In the non-ergodic case, the set is smaller. We are able to prove that this kind of averaging over all possible configurations of the molecules in the ergodic case is able to remove the signature of a correlation that was present in the dynamics of an isolated cluster in reciprocal space, *i.e.* we recover the result for a single molecule. In the non-ergodic case, we average over a smaller set of possible states. This kind of weaker averaging does not permit us to assert that we would recover the result for a single molecule. That is the result of our paper.

At this point it is perhaps instrumental to summarize the situation at the hand of an example. Let us take a linear chain whose $2N$ molecules can take only two orientations (which we can call pseudospins). We suppose that the dynamics is given by some rule that two neighbour sites can flip simultaneously their pseudospins (by twofold rotations). If this rule defines permanent dimers in the sense that only molecules 1+2, 3+4, 5+6, etc. can turn simultaneously, then we are in the presence of a strong correlation. The presence of such dimers is immediately obvious on an instaneous photograph of the system and will leave an unmistakeable fingerprint in the dynamics. That is the case we are all familiar with.

We render the situation far more subtle by allowing the dimers to be dissociated by the effects of overlapping clusters. Let us first consider a simultaneous flip of the molecules on sites 1 and 2 (starting from a completely aligned configuration). That introduces a correlation. Now assume that an analogous flip involving sites 2 and 3 follows. Will this remove the “correlation”, as the “image” of the initial “dimer” has been destroyed? The answer is (here) that some less obvious correlation remains. Due to the construction of the model there will always be an even number of flipped pseudospins. How weak it ever might be, this is a (static) correlation that will never disappear from the model. In fact, due to the persistence of these static correlations, the system is not ergodic and does not fulfil the assumptions that are underlying our paper. But in this very specific case it happens that we can actually prove that the model does *not* yield the same neutron answer as a system with totally uncorrelated molecules. One can easily check this by using our method of calculation on a model with a small (even) number of pseudospins (*e.g.* 4) and exploiting the fact that the configuration space for the uncorrelated case splits into two disjoint subsets when we introduce the dynamical correlations. But if in another type of dynamical model the configuration space were not to split, then we will be able to assert with certainty that the dynamical signal will not offer clues as to the presence of the dynamical correlations.

## 2 Motivation of the use of our method

The reader might find the mathematical leap we will take to configuration space too cumbersome and too much of a fuss to his taste. Is all this really necessary? Part of the answer may reside in the following warning against a possible confusion. Consider the following argument. When we inspect an instantaneous photograph of an ergodic system, the orientations of the molecules will in general look completely random. From this observation it takes only one step to argue that the “correlations are random”. Would that not show that our result is trivial? [7] The problem is that the word “correlation” occurs with several different meanings in this context. The (spatial) *static* correlations between the orientations of the molecules that would be visible in an instantaneous photograph of the sample may well be random[1]. However, the instant *dynamical* (or temporal) correlations are not random, as they tie up a well-defined set of molecules into a cog-wheel.

To avoid confusion, it is thus important to realize that the word correlation can intervene with two entirely different meanings in the discussion and in the mind of the reader. We have *static* orientational correlations between the molecules of the whole crystal that we may detect in a snapshot of the system. We call such snapshots configurations. These static correlations are the ones that matter in structural diffraction techniques. One will run into trouble if one does not properly sort out for oneself that moving to a dynamical context implies that it is no longer these static correlations within one snapshot that are the important quantities: We have to consider *temporal* correlations between *pairs* of such snapshots at *all* possible times. The cog-wheel mechanism defines *dynamical* correlations between molecules within a (small) cluster, in the sense that it tells you which molecules will turn simultaneously and how they will turn. The dynamical correlations are the ones that really count, not the static ones, although the dynamical correlations give of course rise to static correlations. In view of this remark, the loose phrasing "in the presence of correlations" appears thus as fraught with ambiguity.

An important aspect of our method is that it develops a precise mathematical tool that permits to account for all kinds of details that can arise in an argument about correlations in a very clear and rigorous way. The examples of the correlations that persist on a linear chain despite the dissociation of the dimers and of the fallacy based on the ambiguous use of the phrasing "random correlation" as sketched above may serve to show how dangerous it is to underestimate the difficulty of deciding on one's mere intuition if a correlation is present within a system or otherwise, and how discussing such matters in informal language can seed confusion.

## 3 Possible domains of application of this work

### 3.1 Scope of experimental probes

We are presenting our work in terms of a coherent neutron scattering problem, but the formalism will also apply to other microscopic techniques, provided the scattering is really coherent and the technique allows to obtain a $Q$-dependence. Coherent scattering does not only occur with neutrons when the nuclei have an important coherent scattering cross-section. In contrast with neutron scattering, where the nuclei can have both a coherent and an incoherent scattering cross section, X-ray and light scattering processes move the electrons and will *uniquely* lead to coherent scattering. Good candidates for applications are thus also quasielastic X-ray scattering and light scattering. In such techniques the $Q$-range tends to be small ($Q \approx 0$), but a lot of progress has been made in the last decade in inelastic X-ray scattering techniques using synchrotron radiation, rendering available large $Q$-values combined with good energy resolution (≈1 meV) [9]. When there is no energy information, the energy-integrated quasielastic scattering will still yield the $\mathbf{Q}$-dependence of the diffuse scattering.

Extremely high resolutions can be obtained with the so-called speckle technique which allows one to study relaxation on a time scale of the order of 15 minutes [10]! Very good resolutions (neV) can also be obtained by nuclear resonance methods using synchrotron radiation [11] (*e.g.* exciting the 14.41 keV Mössbauer level of $^{57}$Fe), but in general this is an incoherent process (as in this process the radiation is temporarily absorbed exciting a nucleus rather than instantaneously re-emitted by the electrons as dipole radiation). Under certain experimental conditions the process can nonetheless be coherent, but then the quasielastic scattering has to be detected against a very strong background of elastic scattering.

### 3.2 Scope of experimental phenomena

Coherent quasielastic neutron scattering studies are rare and this is certainly due to the difficulty of treating the problem theoretically. Incoherent quasielastic neutron scattering can often be modeled by a system of coupled rate equations, that one can solve analytically. But describing correlations, as probed by coherent quasielastic scattering, along such lines proves difficult. One solution to this problem is to drop the ideal of an analytical description all together and to make Monte Carlo [12] or molecular dynamics [13] simulations, but then fitting some variable parameters of the model to the experimental data will no longer be possible.

There are two main categories of stochastic motion that lead to (non-magnetic) quasielastic scattering, *viz.* translational diffusion and rotational relaxation[2]. Our paper does not deal with translational diffusion. There exists a generalization of the Chudley-Eliott model that permits to calculate the coherent quasielastic neutron scattering signal for translational jump diffusion on a lattice. But this is an average description in that it is based on rate equations which rely on the assumption that the concentrations are rigorously homogeneous throughout the sample [15]. For the sake of completeness we refer the reader interested in theoretical aspects of translational diffusion to references [12] and [16]. The bulk of the experimental efforts have focused on the diffusion of D in NbD$_x$ [17] and other metals [18], Ag in silver halides [19] and in Ag$_2$Se [20], Rb in RbAg$_4$I$_5$ [21], Na in Na$_3$PO$_4$ [22], Li in Li$_2$SO$_4$ [23] or in LiAlSiO4 [24], oxygen in UO$_2$ [25], F in fluorites [26], various molecules in zeolithes [27], vacancies in zirconia-stabilized Y$_2$O$_3$ [28], Ga [29] in grain boundary layers, and Cl in SrCl [30].

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[1] In diffraction studies static correlations lead to diffuse scattering. [8] It is perhaps tempting to invert this implication in the sense that absence of static correlations implies absence of diffuse scattering, but this is not correct in the dynamical problem.

[2] In molecular liquids both occur simultaneously and they can be coupled [14].

What kinds of rotational relaxation is our paper then able to address? Let us immediately state that our model may not have a perfect counterpart in the real world, in the sense that the correlations that occur in a real system might be slightly different from what we are able to cover by our assumptions (see *e.g.* the remark on $CD_3H$ below). It is a requirement of not breaking translational symmetry in configuration space that imposes the underlying assumptions of our paper. If these are not met, the calculation of the correlations becomes of a difficulty that is far beyond the methods we use.

We noted at the beginning of the Introduction that the rotating molecules do not need to have the symmetry of the potential wherein they perform the rotational jumps. This is important. If the symmetry of the molecules is the same as the symmetry of the jump, then the sample will look the same after the jump as before the jump. This means that the Fourier transform of the molecules can be factorized out in the calculations and we do not need to go through the more difficult approach of our paper[3].

Combining these two limitations of feasibility and technical interest, the geometry of the nonadecane molecules is instrumental for visualizing the problem that we can treat, and for describing the (restricted) kind of correlations that we have in mind. The physical correlations between the nonadecane molecules that are really experimentally observed in the urea inclusion compound are of a different nature [34], which we are unable to treat (although this was not yet clear at the time we started this work). But this kind of correlations could exist in another system. The major lesson from our exercise must be that we give a non-trivial counter-example that indicates how coherent quasielastic neutron scattering may not always yield the information one expects on the basis of commonly accepted notions.

In our method the configuration space for the single-molecule dynamics is one-dimensional. It is however possible to generalize the formalism such as to recover also higher-dimensional single-molecule configuration spaces[4]. This broadens the scope of possible applications further to three-dimensional rotations of molecules whose symmetry is not the same as that of the rotation symmetry. An example of such cases would be the rotational jumps of molecules of tetrahedral symmetry containing different isotopes (such that the symmetry is broken) as *e.g.* $CH_3D$, $CD_3H$, $CH_2D_2$, $NH_3D$, $C^{79}Br_3{}^{81}Br$, $C^{79}Br_2{}^{81}Br_2$ [31], $CBr_2Cl_2$ [35], $CBrCl_3$ [35], etc. However in the physical world these molecules do not necessarily give rise to solids where our type of problems are encountered. In partially deuterated methane the physics is just different: Bulk $CH_3D$ and $CD_3H$ are either close to rotational diffusion, or there is quantum behaviour. In partially deuterated ammonia, the existence of exchange of $D$ and $H$ between the molecules complicates the picture.

Also octahedral molecules could be considered[5]. Finally, an important application of our result could be $C_{60}$. The (coherent) quasielastic neutron scattering signal of the rotational dynamics of this molecular crystal in its room temperature phase has been successfully described in terms of a model of completely independent rotors by Neumann *et al.* [36]. Although our results have been derived for rotational jumps rather than for continuous rotations as occur in $C_{60}$, they suggest by analogy that it cannot be claimed with certainty on the basis of the sole neutron data of Neumann *et al.* that the molecules would be totally independent.

## 4 Method

The general method we use has been already described previously [1,5]. The idea is to formulate the problem in configuration space. The instantaneous configuration of the whole system is an abstract particle that diffuses on a network in this configuration space. The vertices of the network are the possible configurations of the system. When one single particle of the system makes a jump with a relaxation time $\tau$, we say that the system "jumps" between two configurations with the relaxation time $\tau$. Two configurations that are linked by such a move of one particle are connected by a line of the network carrying a label $\tau$. The dynamics of our system is this way mapped isomorphically onto the problem of the diffusion of a single abstract particle (the system) on a network in configuration space. The only difference is that the embedding configuration space is of considerably higher dimension than physical space.

The physical problem can thus be described in terms of a set of coupled rate equations $\frac{\mathrm{d}}{\mathrm{d}t}\mathbf{P} = \frac{1}{\tau}\mathbf{MP}$, where the column vector $\mathbf{P}(t)$ contains the probabilities $p_{\mathbf{c}}(t)$ that the system is in configuration $\mathbf{c}$ at time $t$, $\tau$ is a relaxation time, and $\mathbf{M}$ is the so-called jump matrix. The Van Hove formalism deals however with probabilities for particles:

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

Here $b_j^{(coh)}$ is the coherent scattering length of nucleus $j$. The indices $j$ et $k$ run through all the nuclei of the physical system considered. These nuclei are situated at position vector $\mathbf{r}_j(t)$ at time $t$; $\hbar\mathbf{k}_i$, $\hbar\mathbf{k}_f$ are the initial and final momentum vectors of the scattered neutron and $\mathbf{Q} = \mathbf{k}_f - \mathbf{k}_i$ is the momentum transfer; $\hbar\omega = E_f - E_i$ is the energy transfer. Finally, $\langle\cdot\rangle_{th}$ stands for a thermal

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[3] Unless the dynamics is more complicated than a simple rotational jump model, due to supplementary problems such as translation-rotation coupling [31–33] etc.

[4] We will not give this derivation in order not to burden the paper. The proof runs as for the one-dimensional case *mutatis mutandis.*

[5] A good example would be $SF_6$, if it were not that the natural element fluorine is mono-isotopic ($^{19}F$), such that the simplification mentioned above can be applied [32].

average. The total scattering function is defined by:

$$\begin{aligned} S(\mathbf{Q},\omega) &= \frac{1}{2\pi}\int_{-\infty}^{\infty} \mathrm{e}^{-\imath\omega t}\sum_{j,k}\langle \mathrm{e}^{\imath\mathbf{Q}\cdot(\mathbf{r}_k(t)-\mathbf{r}_j(0))}\rangle_{th}\,\mathrm{d}t \\ &= \frac{1}{2\pi}\int_{-\infty}^{\infty} \mathrm{e}^{-\imath\omega t}\, S(\mathbf{Q},t)\,\mathrm{d}t. \end{aligned} \tag{2}$$

It is the spatio-temporal Fourier transform of the Van Hove correlation function, which expresses the probability to find a particle at $\mathbf{r}$ at time $t$ if the same or another particle is present at $\mathbf{0}$ at time 0:

$$S(\mathbf{Q},\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} \mathrm{e}^{-\imath\omega t}\sum_{j,k} b_j^*\, b_k\langle \mathrm{e}^{\imath\mathbf{Q}\cdot(\mathbf{r}_k(t)-\mathbf{r}_j(0))}\rangle_{th}\mathrm{d}t \tag{3}$$

where we have taken the liberty to include the scattering lengths into the definition of $S$. To make contact with a formalism based on configurations we define

$$\begin{aligned} \mathcal{F}(\mathbf{Q},t) &= \sum_k b_k\; \mathrm{e}^{\imath\mathbf{Q}\cdot\mathbf{r}_k(t)} \\ &= \frac{1}{(2\pi)^3}\int_{\mathbb{R}^3} \mathrm{e}^{\imath\mathbf{Q}\cdot\mathbf{r}}\sum_k b_k\cdot\delta(\mathbf{r}-\mathbf{r}_k)\,\mathrm{d}\mathbf{r} \end{aligned} \tag{4}$$

then

$$\sum_{j,k} b_j^*\, b_k\,\langle \mathrm{e}^{\imath\mathbf{Q}\cdot(\mathbf{r}_k(t)-\mathbf{r}_j(0))}\rangle_{th} = \langle\mathcal{F}(\mathbf{Q},t)\,\mathcal{F}^*(\mathbf{Q},0)\rangle_{th} \tag{5}$$

where $\mathcal{F}(\mathbf{Q},t)$ is nothing else than the spatial Fourier transform of a configuration of Dirac measures of weight $b_k$ put into the positions $\mathbf{r}_k$. We obtain then:

$$S(\mathbf{Q},\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} \mathrm{e}^{-\imath\omega t}\,\langle\mathcal{F}(\mathbf{Q},t)\,\mathcal{F}^*(\mathbf{Q},0)\rangle_{th}\,\mathrm{d}t. \tag{6}$$

The thermal average is:

$$\langle\mathcal{F}(\mathbf{Q},t)\,\mathcal{F}^*(\mathbf{Q},0)\rangle_{th} = \sum_{j,k}\mathcal{F}_j(\mathbf{Q})\,p_{j,k}(t)\,\mathcal{F}_k^*(\mathbf{Q}). \tag{7}$$

In contrast with the preceding equations the dummy variables $j,k$ are now running over all possible configurations rather than over all nuclei; $p_{j,k}(t)$ are the probabilities that the system is in configuration $j$ at time $t$ if it was in configuration $k$ at time 0. The formal solution is worked out in reference [1] and does not contain further surprising steps or new ideas: By diagonalizing $\mathbf{M} = \mathbf{S}\,\Lambda\,\mathbf{S}^{-1}$, we can write the solution of this set of coupled linear differential equations as $\mathbf{P}(t) = \mathbf{S}\,\exp{(\Lambda t/\tau)}\,\mathbf{S}^{-1}\,\mathbf{P}(0)$. By plugging in the various initial conditions into $\mathbf{P}(0)$, we obtain then the full set of probabilities $p_{j,k}(t)$ that the system is in configuration $j$ at time $t$ if it was in configuration $k$ at time 0. As already stated, these are the quantities that are needed. For the thermal averaging we must consider all possible initial configurations $\mathbf{P}(0)$. (All these column vectors can be compounded into a square matrix, which in general will be a multiple of the unit matrix.) A proper choice of initial conditions will also take into account the thermal occupation factors, *i.e.* entail the required thermal averaging. The total scattering function is obtained from the spatio-temporal Fourier transform of the thermal average of the correlation functions. By writing in addition the right hand side of equation (7) in matrix form, we obtain the final expression for the total scattering function, which reads: $S(\mathbf{Q},\omega) = \frac{1}{n^N}\,\mathbf{F}\,\mathbf{S}\;\mathcal{F}(\,\mathrm{e}^{\Lambda t/\tau}\,)\;\;\mathbf{S}^{\dagger}\,\mathbf{F}^{\dagger}$, where $\mathbf{F}$ is the row matrix that contains the spatial Fourier transforms $\mathcal{F}_{\mathbf{c}}(\mathbf{Q})$ of the configurations $\mathbf{c}$ (obtained by putting a Dirac measure of weight $b_x$ at the position of each atom of type $x$ as explained above); $\mathcal{F}$ in $\mathcal{F}(\,\mathrm{e}^{\Lambda t/\tau}\,)$ stands for the temporal Fourier transform. The normalization factor $\frac{1}{n^N}$ is here written for the case of uncorrelated $n$-fold rotational jumps of $N$ molecules.

## 5 Formulation of the jump matrix

When there are no correlations between the molecules, the configuration space for the $n$-fold rotational jumps of $N$ molecules on a lattice $\mathcal{L}\subset\mathbb{R}^d\,(d\in\{1,2,3\})$, *e.g.* $\mathcal{L} = (\,[1,\ell]\cap\mathbb{N}\,)^d$, $N=\ell^d$, will be a hypercubic lattice [37] $\mathcal{H} = (\mathbb{Z}/n\,)^N$ with cyclic boundary conditions in $\mathbb{R}^N$. (Each particle adds one dimension to configuration space: *E.g.* if there were just two molecules ($N=2$) that make threefold rotational jumps ($n=3$), the configuration space would be the square lattice of the $n^N = 3^2 = 9$ points $(1,1),(1,2),...(i,j),...(3,3)$. The configuration $(i,j)$ corresponds then to the situation that particle 1 has orientation $i$ and particle 2 orientation $j$. The boundary conditions are cyclic as each particle can go through the successive orientations $1\rightarrow 2\rightarrow 3\rightarrow 1$ as the particles never collide. This is different for translational motions, for which the configuration space therefore has boundaries. It is for this reason that our approach cannot be applied for translational motion.) For a three-dimensional sample ($d=3$), the position vectors of the molecules will be $(\,j_x,j_y,j_z\,)\in\mathcal{L}$. The jump matrix $\mathbf{M}$ is then defined by:

$$M_{\mathbf{c};\mathbf{d}} = -2N\,\delta_{\mathbf{c};\mathbf{d}} + \sum_{\mathbf{j}\,\in\,\mathcal{L}}\left(\,\delta_{\mathbf{c};\mathbf{d}+\mathbf{e_j}} + \delta_{\mathbf{c};\mathbf{d}-\mathbf{e_j}}\,\right). \tag{8}$$

The reader should not feel intimidated by the few very concise notations of this type that occur in the paper. They are mainly given for the sake of completeness. The main point he should capture is at which points in the jump matrix there are non-zero entries and how they look like. Equation (8) is built up as follows. There is a unit vector $\mathbf{e_j}$ in hypercubic space associated with each molecule (with position vector $\mathbf{j}$) that can turn: As we illustrated with the example of two particles above, each molecule adds a dimension to configuration space. When we start from a configuration $\mathbf{c}$ and the molecule $\mathbf{j}$ makes a rotational jump, the system goes to the configuration $\mathbf{d} = \mathbf{c}+\mathbf{e_j}$. Hence, in the absence of correlations, a configuration $\mathbf{c}\in\mathcal{H}$ has $2N$ neighbours $\mathbf{d} = \mathbf{c}\pm\mathbf{e_j}$, where $\mathbf{j} = (\,j_x,j_y,j_z\,)\in\mathcal{L}$: At the line corresponding to $\mathbf{c}$ in the jump matrix there are thus non-zero entries at all columnar positions corresponding to the configurations $\mathbf{d}=\mathbf{c}+\mathbf{e}_{\mathbf{j}}$ and $\mathbf{d}=\mathbf{c}-\mathbf{e}_{\mathbf{j}}$, a fact which is expressed through the presence of the Kronecker delta's $\delta_{\mathbf{c};\mathbf{d}+\mathbf{e}_{\mathbf{j}}}$ and $\delta_{\mathbf{c};\mathbf{d}-\mathbf{e}_{\mathbf{j}}}$. The diagonal terms follow from these terms as in any other jump matrix for a diffusion problem.

The unit vectors $\mathbf{e}_{\mathbf{j}}$ are the generators of the hypercubic lattice $\mathcal{H}$, and each configuration $\mathbf{c}$ accessible can be written as $\mathbf{c}=\sum_{\mathbf{j}} c_{\mathbf{j}}\, \mathbf{e}_{\mathbf{j}}$, with $c_{\mathbf{j}} \in \mathbb{Z}/n$. The hypercubic lattice $\mathcal{H}$ represents all possible configurations that can be obtained by $n$-fold rotations, and therefore the configuration space when there are correlations will be a sublattice $\mathcal{S} \subset \mathcal{H}$ of $\mathcal{H}$[6].

It is logical that we assume that due to the range of the intermolecular interactions, the set or cluster of jumping molecules extends to a neighbour shell of a certain order. Due to the translational invariance on the physical lattice $\mathcal{L}$, this cluster should be allowed to occur at every lattice site $\mathbf{j} \in \mathcal{L}$. A configuration $\mathbf{c}$ will now be connected to other configurations $\mathbf{c}\pm\mathbf{v}_{\mathbf{j}}, \mathbf{j} \in \mathcal{L}$ on the sublattice $\mathcal{S}$, than $\mathbf{c}\pm\mathbf{e}_{\mathbf{j}}, \mathbf{j} \in \mathcal{L}$ as for the independent dynamics, and it is the set of $\nu$ relative position vectors $\mathbf{v}_{\mathbf{j}}$ that has to be defined. *E.g.* if on a two-dimensional square lattice $\mathcal{L} = (\,[1,\ell] \cap \mathbb{N}\,)^2$ with cyclic boundary conditions, the jump of a molecule at $(\,j_x, j_y\,)$ over $2\pi/n$ is always accompanied by opposite jumps over $-2\pi/n$ of its four first neighbours, then $\nu = \ell^2$ and

$$\begin{aligned}\mathbf{v}_{(j_x,j_y)} = \mathbf{e}_{(j_x,j_y)} - \mathbf{e}_{(j_x+1,j_y)} - \mathbf{e}_{(j_x-1,j_y)} \\ - \mathbf{e}_{(j_x,j_y+1)} - \mathbf{e}_{(j_x,j_y-1)}, \forall(\,j_x, j_y\,) \in \mathcal{L},\end{aligned} \qquad (9)$$

where the minus signs translate the fact that the rotations are opposite. We can understand this by decomposing the combined move into a succession of single-molecule jumps: We first turn the molecule $(j_x, j_y)$, which changes the configuration from $\mathbf{c}$ to $\mathbf{c}+\mathbf{e}_{(j_x,j_y)}$. Then we turn the molecule $(j_x+1, j_y)$, which changes the configuration further from $\mathbf{c}+\mathbf{e}_{(j_x,j_y)}$ to $\mathbf{c}+\mathbf{e}_{(j_x,j_y)}-\mathbf{e}_{(j_x+1,j_y)}$, etc... upto the final configuration $\mathbf{c}+\mathbf{v}_{(j_x,j_y)}$. The order in which we take these individual moves is not important, as in the combined move of the five molecules the system does not visit the intermediate configurations and goes immediately from the initial ($\mathbf{c}$) to the final configuration ($\mathbf{c}+\mathbf{v}_{(j_x,j_y)}$). On our network there will be a line that connects these two configurations and which will be labeled by $\tau$. *Of course the relaxation time $\tau$ we use now has no longer any relationship whatsoever with the relaxation times we used in the problem of independent dynamics.* It is the relaxation time for a cluster, not for a molecule, and the probabilities we are dealing with here can in principle not be expressed as a product of probabilities as would occur if the rotors were independent[7]. The $\nu = \ell^2$ vectors $\mathbf{v}_{\mathbf{j}}$, $\mathbf{j} = (\,1,1\,), (\,1,2\,), \ldots (\,\ell,\ell\,)$ are the generators of the sublattice $\mathcal{S}$. Using the hypercubic norm, we see that $\|\, \mathbf{v}_{(j_x,j_y)} \,\| = 5$.

As a second example, we could also imagine that each molecule at $(j_x, j_y)$ has (for symmetry reasons) four equivalent alternatives to jump simultaneously with a single first neighbour. Then $\nu = 4\,\ell^2$ and $\forall (j_x, j_y) \in \mathcal{L}$:

$$\begin{aligned}\mathbf{v}_{(j_x,j_y),1} &= \mathbf{e}_{(j_x,j_y)} - \mathbf{e}_{(j_x+1,j_y)}, \\ \mathbf{v}_{(j_x,j_y),2} &= \mathbf{e}_{(j_x,j_y)} - \mathbf{e}_{(j_x-1,j_y)}, \\ \mathbf{v}_{(j_x,j_y),3} &= \mathbf{e}_{(j_x,j_y)} - \mathbf{e}_{(j_x,j_y+1)}, \\ \mathbf{v}_{(j_x,j_y),4} &= \mathbf{e}_{(j_x,j_y)} - \mathbf{e}_{(j_x,j_y-1)}.\end{aligned} \qquad (10)$$

Here $\|\, \mathbf{v}_{(j_x,j_y),r} \,\| = 2$ ( $r \in \{1,2,3,4\}$ ). We see thus that in the general situation with correlations the jump matrix $\mathbf{M}$ will be defined by

$$M_{\mathbf{c};\mathbf{d}} = -2N\rho\, \delta_{\mathbf{c};\mathbf{d}} + \sum_{\mathbf{j} \in \mathcal{L}} \sum_{r=1}^{\rho} \left(\, \delta_{\mathbf{c};\mathbf{d}+\mathbf{v}_{\mathbf{j},r}} + \delta_{\mathbf{c};\mathbf{d}-\mathbf{v}_{\mathbf{j},r}} \,\right), \qquad (11)$$

where $\rho = \nu/\ell^d$ is the number of different types $r$ of clusters per lattice site that can turn (i.e. $\rho = 4$ in the example of Eq. (10)). The definition of equation (11) is analogous to the one in equation (8) with each vector $\mathbf{e}_{\mathbf{j}}$ replaced by $\rho$ vectors $\mathbf{v}_{\mathbf{j},r}$. We can more generally assume that the various possibilities labeled by $r$ lead to different time constants. Drawing in the time constants into $\mathbf{M}$ the jump matrix becomes:

$$M_{\mathbf{c};\mathbf{d}} = \sum_{r=1}^{\rho} \frac{1}{\tau_r} \left( -2N\delta_{\mathbf{c};\mathbf{d}} + \sum_{\mathbf{j}\in\mathcal{L}} \left( \delta_{\mathbf{c};\mathbf{d}+\mathbf{v}_{\mathbf{j},r}} + \delta_{\mathbf{c};\mathbf{d}-\mathbf{v}_{\mathbf{j},r}} \right) \right). \qquad (12)$$

This notation can be further generalized by noticing that $r$ corresponds to a difference (or translation) vector $\mathbf{t} \in \mathcal{L}$, $\sum_r \to \sum_{\mathbf{t}\in\mathcal{L}}$. We must then admit that for many values of $\mathbf{t}$, we will have $\frac{1}{\tau_{\mathbf{t}}} = 0$, or replace $\mathbf{t} \in \mathcal{L}$ by $\mathbf{t} \in \mathcal{G}$ where $\mathcal{G}$ is a physical cluster:

$$M_{\mathbf{c};\mathbf{d}} = \sum_{\mathbf{t}\in\mathcal{G}} \frac{1}{\tau_{\mathbf{t}}} \left( -2N\delta_{\mathbf{c};\mathbf{d}} + \sum_{\mathbf{j}\in\mathcal{L}} \left( \delta_{\mathbf{c};\mathbf{d}+\mathbf{v}_{\mathbf{j},\mathbf{t}}} + \delta_{\mathbf{c};\mathbf{d}-\mathbf{v}_{\mathbf{j},\mathbf{t}}} \right) \right). \qquad (13)$$

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[6] We would like to stress that there is no underlying assumption related to representing the various configurations as points on a hypercubic lattice, for the mere convenience of enumerating them more easily. This also true when the rotors are not independent. More specifically, it does not imply any factorization of probabilities as we would have in the case of independent rotors. The probabilities will be given by the topological connectivity of the network or graph that links these points. These lines could be very different from the edges of the hypercubes of the hypercubic lattice that occur in the case of independent dynamics. The probability for a jump between two configurations is taken into account by connecting the points that represent them by a line labeled with its relaxation time. Only if these probabilities themselves were factorized would we have an underlying independence.

[7] It must be obvious that the occurrence of a cluster is probabilistic: The model of equation (9) is perhaps best seen as part of a larger model wherein *e.g.* a molecule has some probability to turn alone, some probability to turn as given by equation (9), and some probabilities to turn even within other types of clusters (see *e.g.* Eq. (20) below).

$$\begin{aligned}
\lambda_{\mathbf{k}} = -2\ell^2 &+2\cos\left[\frac{2\pi}{n}\left(k_{(1,1)} - k_{(1,2)} - k_{(1,\ell)} - k_{(2,1)} - k_{(\ell,1)} + 3\right)\right] \\
&+2\cos\left[\frac{2\pi}{n}\left(-k_{(1,1)} + k_{(1,2)} - k_{(1,3)} - k_{(2,2)} - k_{(\ell,2)} + 3\right)\right] \\
&\qquad\vdots \\
&+2\cos\left[\frac{2\pi}{n}\left(k_{(j_x,j_y)} - k_{(j_x+1,j_y)} - k_{(j_x-1,j_y)} - k_{(j_x,j_y+1)} - k_{(j_x,j_y-1)} + 3\right)\right] \\
&\qquad\vdots \\
&+2\cos\left[\frac{2\pi}{n} - k_{(1,\ell)} - k_{(\ell-1,\ell)} - k_{(\ell,1)} - k_{(\ell,\ell-1)} + k_{(\ell,\ell)} + 3\,)\right],
\end{aligned} \tag{15}$$

We have just given some examples of possible correlations. In the present paper we will not further insist on writing down a general formalism that would cover all possible cases. First of all, there are too many possibilities. Secondly, we think that a general abstract formalism in configuration space [38] (which typically has a dimension $\approx 10^{24}$) with notations of the rather elaborate type that occur in equation (11–13), might easily conceal the rather simple ideas behind our method. We will therefore rather proceed by illustrating the method for examples of the type given, in order to familiarize us with its spirit.

## 6 The problem of ergodicity

Since the hypercubic norms of the vectors $\mathbf{v}_{\mathbf{j}}$ are by definition larger than 1 in the presence of correlations, one would be inclined to think that $\mathcal{S}$ will always be a *strict* subset of $\mathcal{H}$, which we expressed by saying that our dynamical problem is no longer "ergodic". The real situation is more subtle. Taking the possibility of non-ergodicity seriously is a difficult task that we are unable to treat rigorously in general. One can develop a physical argument to put forward the idea that we can relax the condition of ergodicity to a weaker criterium of *local* (as opposed to *global*) ergodicity. For the main stream of the paper we will henceforth assume ergodicity. But despite the fact that we devote here only a few lines to this assumption, we must stress that ergodicity is a vital issue for the validity of the calculations in the rest of the paper.

## 7 Solution of the jump model in the ergodic case

When the system is ergodic, we can immediately use the eigenvectors we already established for $\mathcal{H}$ in reference [1], and we will be able to derive without effort the eigenvalues from the form of $\mathbf{v}_{\mathbf{j},r}$, $\mathbf{j} \in \mathcal{L}$. Indeed, when the system is ergodic then the jump matrix in configuration space has translational symmetry along each of the directions defined by the $N$ unit vectors $\mathbf{e}_{\mathbf{j}}$ that span $\mathcal{H}$. The eigenvectors are therefore just $N$-dimensional Bloch waves, *i.e.* $n^N \times 1$ column matrices $\mathbf{V}^{(\mathbf{k})}$ defined by $[\,\mathbf{V}^{(\mathbf{k})}\,]_{\mathbf{c}} = \exp[\,\imath\,\frac{2\pi}{n}\,(\mathbf{k}-\mathbf{k}_0)\cdot(\mathbf{c}-\mathbf{k}_0)\,], \forall \mathbf{c} \in \mathcal{H}$. Here $\mathbf{k}_0$ stands for $(1,1,1,\ldots 1,1) \in \mathbb{R}^N$ and is introduced to take into account the fact that the expression for the eigenvectors features the quantities $k_\xi$ and $c_\xi$ always under the form of linear combinations $(k_\xi - 1)$, and $(c_\xi - 1)$. The $N$-dimensional Bloch wave is obtained as a Kronecker product of $N$ one-dimensional Bloch waves, just as a three-dimensional phonon can also be written as a Kronecker product of three one-dimensional Bloch-waves. (Each one-dimensional Bloch wave is a $n \times 1$ column matrix.) Combining these eigenvectors with the definition of the $n^N \times n^N$ jump matrix $\mathbf{M}$ in equation (11) yields the corresponding eigenvalues:

$$\lambda_{\mathbf{k}} = -2\rho N + 2\sum_{\mathbf{j}\,\in\,\mathcal{L}}\ \sum_{r=1}^{\rho} \cos\left[\,\mathbf{v}_{\mathbf{j},r}\cdot(\,\mathbf{k}-\mathbf{k}_0\,)\,\right]. \tag{14}$$

This is exactly analogous to the way the eigenvalues of a phonon problem are obtained by operating the dynamical matrix on the Bloch wave eigenvectors. We just calculate $\mathbf{M}\mathbf{V}^{(\mathbf{k})}$ using the definitions of $\mathbf{M}$ and $\mathbf{V}^{(\mathbf{k})}$ and check that the result can be rewritten as $\lambda^{(\mathbf{k})}\,\mathbf{V}^{(\mathbf{k})}$ for some value $\lambda^{(\mathbf{k})}$. For the phonon case in text books, this calculation is usually only written for a general line of the column matrix that represents the eigen vector, with the possible effect that the argument might not be recognized as perfectly analogous to the one we are dealing with here. *E.g.* in the case of equation (9) we have $N = \ell^2$, $\rho = 1$, $\forall \mathbf{j} \in \mathcal{L}$ : $\mathbf{k}_0 \cdot \mathbf{v}_{\mathbf{j}} = -3$, such that equation (14) is more explicitly seen to yield

*see equation (15) above,*

where $\mathbf{k} = (\,k_{(1,1)}, k_{(1,2)}, \ldots k_{(j_x,j_y)}, \ldots k_{(\ell,\ell)}\,)$, and $k_{(j_x,j_y)} \in \mathbb{Z}/n$. There are thus $n^{\ell^2}$ $\mathbf{k}$-vectors in the case of equation (9). In fact, a general configuration $\mathbf{c}$ has $\ell^2$ vector components: $\mathbf{c} = (c_{(1,1)}, c_{(1,2)}, \cdots c_{(j_x,j_y)}, \cdots c_{(\ell,\ell)})$. The coordinates $c_{(j_x,j_y)}$ can take $n$ values representing the $n$ possible orientations of the molecule at $(j_x, j_y) \in \mathcal{L}$. There are thus in total $n^{\ell^2}$ configurations, and for each of them there is a probability. The jump matrix $\mathbf{M}$ works on the space of these $n^{\ell^2}$ configurations. An eigenvector $\mathbf{V}^{(\mathbf{k})}$ is a vector with $n^{\ell^2}$ entries $[\,\mathbf{V}^{(\mathbf{k})}\,]_{\mathbf{c}}$, where $\mathbf{c}$ runs through all possible configurations. We can thus depicture $\mathbf{V}^{(\mathbf{k})}$ as a function (the Bloch wave): $\mathbf{V}^{(\mathbf{k})} : \mathbf{c} \rightarrow [\,\mathbf{V}^{(\mathbf{k})}\,]_{\mathbf{c}}$. Let us operate $\mathbf{M}$ on an eigenvector. The first non-zero off-diagonal entry in $\mathbf{M}$ corresponds to the possibility that $\mathbf{c}$ undergoes a transformation to $\mathbf{c} + \mathbf{v}_{(1,1)}$. That will transform the function from $\exp[\,\imath\,\frac{2\pi}{n}\,(\mathbf{k}-\mathbf{k}_0)\cdot(\mathbf{c}-\mathbf{k}_0)\,], \forall\mathbf{c} \in \mathcal{H}$ to $\exp[\,\imath\,\frac{2\pi}{n}\,(\mathbf{k}-\mathbf{k}_0)\cdot(\mathbf{c}+\mathbf{v}_{(1,1)}-\mathbf{k}_0)\,], \forall\mathbf{c} \in \mathcal{H}$, i.e. multiply it by $\exp[\,\imath\frac{2\pi}{n}(\,k_{(1,1)} - k_{(1,2)} - k_{(1,\ell)} - k_{(2,1)} - k_{(\ell,1)} + 3\,)\,]$. Continuing this way with the possible transformations towards $\mathbf{c} + \mathbf{v}_{(1,2)}$,..., $\mathbf{c} + \mathbf{v}_{(\ell,\ell)}$, including also the possible transformations towards $\mathbf{c} - \mathbf{v}_{(1,1)}$, $\mathbf{c} - \mathbf{v}_{(1,2)}$,..., $\mathbf{c} - \mathbf{v}_{(\ell,\ell)}$, and finally adding the diagonal term we obtain the result announced in equation (15).

The whole part of the calculation involving the determination of the structure factors remains the same as for the case without correlations. In fact this calculation (based on the evaluation of $\mathbf{G} = \mathbf{F}\,\mathbf{S}$) is entirely defineded by the values of the eigenvectors ($\mathbf{S}$) and the Fourier transforms of the configurations ($\mathbf{F}$) and these are not changed in the ergodic case. This means that equations (35, 37) of reference [1] remain valid. Using the same notations as in that paper, the Lorentzian $L(\hbar\lambda_{\mathbf{k}}/\tau, \omega)$ will be associated with $|\,G_{\mathbf{k}}\,|^2$, where

$$G_{k_{(1,1)};k_{(1,2)};\ldots k_{(j_x,j_y)};\ldots k_{(\ell,\ell)}} = \frac{1}{n}\sum_{j_x=1}^{\ell}\sum_{j_y=1}^{\ell}\sum_{c_{(j_x,j_y)}=1}^{n} F_{c_{(j_x,j_y)}}\,\mathrm{e}^{\imath\frac{2\pi}{n}(c_{(j_x,j_y)}-1)(k_{(j_x,j_y)}-1)} \times \mathrm{e}^{\imath\mathbf{Q}\cdot\mathbf{r}_{(j_x,j_y)}}\,\delta_{1k_{(1,1)}}\delta_{1k_{(1,2)}}\ldots\delta_{1k_{(j_x,j_y-1)}} \times\ \delta_{1k_{(j_x,j_y+1)}}\ldots\delta_{1k_{(\ell,\ell-1)}}\delta_{1k_{(\ell,\ell)}}. \quad (16)$$

Here $F_{c_{(j_x,j_y)}}$ is the Fourier transform of the molecule $(j_x, j_y)$ (with orientation $c_{(j_x,j_y)}$) if it were placed at the origin. (The real position vector of this molecule is $\mathbf{r}_{(j_x,j_y)}$.) Consequently, the structure factor of the elastic term remains the same. The structure factors of the quasielastic terms remain also the same. Just the widths of the Lorentzians have to be re-examined. Due to the presence of the Kronecker symbols in equation (16) only Lorentzians for $\mathbf{k}$-values which have one single component $k_{(j_x,j_y)} \neq 1$ are contributing. In our example on the square lattice, these are the Lorentzians with

$$\lambda_{\mathbf{k}} = -2\ell^2 + 2\,(\ell^2 - 5) + 10\,\cos\left[\frac{2\pi}{n}(\,k_{(j_x,j_y)} - 1\,)\right], \quad (17)$$

since in $\lambda_{\mathbf{k}}$ there are $\ell^2 - 5$ terms with a vanishing argument in the cosines and 5 terms where the argument of the cosines collapse to $\frac{2\pi}{n}(\,k_{(j_x,j_y)} - 1\,)$. We recover thus the same Lorentzians with a width parameter $-2+2\cos[\,\frac{2\pi}{n}(\,k_{(j_x,j_y)}-1\,)\,]$ as in the case without correlations, except for the detail that the relaxation time $\tau$ that occurs in the rate equations is being replaced in the final result by a five times faster relaxation time $\tau/5$, which does not happen in the case without correlations[8]. *With respect to the independent dynamics, the* **Q***-dependences of the intervening Lorentzians remain the same, only the energy widths of the intervening Lorentzians are modified.* Conclusion: In our systems it is absolutely impossible to appreciate from the $\mathbf{Q}$-dependence alone of a signal due to coherent neutron scattering if there are correlations or otherwise! One can only hope that a comparison with incoherent data might still yield some clues. This result will be general if the cardinal number $\#\mathcal{H}$ of the set of possible configurations $\mathcal{H}$ is not altered by the presence of correlations (case (1) in the terminology of the Introduction). In fact, the factor 5 in our example comes from the circumstance that our clusters contain five molecules, such that $\mathbf{v}_{(j_x,j_y)}$ will contain five terms. Due to this $\lambda_{\mathbf{k}}$ will contain five terms that contain $(\,k_{(j_x,j_y)} - 1\,)$, each time combined with other terms of the general type $\pm(\,k_{(j'_x,j'_y)} - 1\,)$, that vanish since $k_{(j'_x,j'_y)} = 1$. All other contributions to $\lambda_{\mathbf{k}}$ are devoid of terms in $k_{(j_x,j_y)}$.

We have not addressed the possibility illustrated by the example of equation (10), where we have more than one type of cluster. In principle this case is not different in nature from the one embodied by equation (9), since there we also have already $\nu > N$, such that equation (9) represents two equations rather than one. Provided we have ergodicity we can derive for this model from equation (11) with $N = \ell^2, \rho = 4$, $(\forall\mathbf{j} \in \mathcal{L})\,(\forall r \in \{1,2,3,4\}\,)\,(\,\mathbf{k}_0\cdot\mathbf{v}_{\mathbf{j},r} = 0\,)$:

*see equation (18) next page.*

Expressing the selection rule from equation (16) that only Lorentzians are contributing which correspond to a $\mathbf{k}$-value that contains a single component $k_{(j_x,j_y)} \neq 1$, we just retain the Lorentzians with

$$\lambda_{\mathbf{k}} = -8\ell^2 + 2\,(4\,\ell^2 - 8) + 16\,\cos\left[\frac{2\pi}{n}\left(\,k_{(j_x,j_y)} - 1\,\right)\right], \quad (19)$$

such that the widths are now again $-2 + 2\cos[\,\frac{2\pi}{n}(\,k_{(j_x,j_y)} - 1\,)]$, this time with a prefactor 8, since there are in total 16 different moves that involve a jump of molecule $(\,j_x, j_y\,)$.

We may note that we have already covered quite realistically looking possibilities. The task of taking into account correlations of this type on a whole lattice definitely

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[8] But since we are dealing with clusters of 5 molecules, we might originally have had the intuition to put a value 5 times slower than in the uncorrelated case into the rate equations. If we do not allow for this, then we would end up with a speed-up of the quasielastic signal in the presence of reorienting clusters, which is quite unphysical, as it should in principle be more difficult to move a set of molecules rather than a single molecule. This use of a factor 5 based on a handwaving argument can only be considered as a first approximation. We have no means to elucidate this relationship any further, since the jump time a single molecule would have had if its jumps had been independent is just not available to the experimentalist. There could be a change in the jump time parameter between the cases of correlated and uncorrelated jumps, but this cannot be learned from an inspection of coherent scattering data alone, since there is no change in the structure factors.

$$\begin{aligned}\lambda_{\mathbf{k}} = -8\ell^2 &+2\cos\left[\frac{2\pi}{n}\left(k_{(1,1)} - k_{(1,2)}\right)\right] + 2\cos\left[\frac{2\pi}{n}\left(k_{(1,1)} - k_{(1,\ell)}\right)\right]\\
&+2\cos\left[\frac{2\pi}{n}\left(k_{(1,1)} - k_{(2,1)}\right)\right] + 2\cos\left[\frac{2\pi}{n}\left(k_{(1,1)} - k_{(\ell,1)}\right)\right]\\
&+2\cos\left[\frac{2\pi}{n}\left(k_{(1,2)} - k_{(1,1)}\right)\right] + 2\cos\left[\frac{2\pi}{n}\left(k_{(1,2)} - k_{(1,3)}\right)\right]\\
&+2\cos\left[\frac{2\pi}{n}\left(k_{(1,2)} - k_{(2,2)}\right)\right] + 2\cos\left[\frac{2\pi}{n}\left(k_{(1,2)} - k_{(\ell,2)}\right)\right]\\
&\qquad\vdots\\
&+2\cos\left[\frac{2\pi}{n}\left(k_{(j_x,j_y)} - k_{(j_x+1,j_y)}\right)\right] + 2\cos\left[\frac{2\pi}{n}\left(k_{(j_x,j_y)} - k_{(j_x-1,j_y)}\right)\right]\\
&+2\cos\left[\frac{2\pi}{n}\left(k_{(j_x,j_y)} - k_{(j_x,j_y+1)}\right)\right] + 2\cos\left[\frac{2\pi}{n}\left(k_{(j_x,j_y)} - k_{(j_x,j_y-1)}\right)\right]\\
&\qquad\vdots\\
&+2\cos\left[\frac{2\pi}{n}\left(k_{(\ell,\ell)} - k_{(1,\ell)}\right)\right] + 2\cos\left[\frac{2\pi}{n}\left(k_{(\ell,\ell)} - k_{(\ell-1,\ell)}\right)\right]\\
&+2\cos\left[\frac{2\pi}{n}\left(k_{(\ell,\ell)} - k_{(\ell,1)}\right)\right] + 2\cos\left[\frac{2\pi}{n}\left(k_{(\ell,\ell)} - k_{(\ell,\ell-1)}\right)\right]. \qquad (18)\end{aligned}$$

seemed daunting before we embarked on our method. The most realistic case would probably involve a distribution of cluster sizes, whereby each cluster has its own characteristic relaxation time. *E.g.* on the square lattice we could instead of equation (9), have relaxation times and clusters $\forall(j_x,j_y)\in\mathcal{L}$:

$$\begin{aligned}\tau_1 : \mathbf{v}_{(j_x,j_y),1} &= \mathbf{e}_{(j_x,j_y)} - \mathbf{e}_{(j_x+1,j_y)} - \mathbf{e}_{(j_x-1,j_y)}\\
&\quad - \mathbf{e}_{(j_x,j_y+1)} - \mathbf{e}_{(j_x,j_y-1)},\\
\tau_2 : \mathbf{v}_{(j_x,j_y),2} &= \mathbf{e}_{(j_x,j_y)} - \mathbf{e}_{(j_x+1,j_y)} - \mathbf{e}_{(j_x-1,j_y)}\\
&- \mathbf{e}_{(j_x,j_y+1)} - \mathbf{e}_{(j_x,j_y-1)} + \mathbf{e}_{(j_x-1,j_y+1)} + \mathbf{e}_{(j_x+1,j_y-1)}\\
&+ \mathbf{e}_{(j_x+2,j_y)} + \mathbf{e}_{(j_x-1,j_y-1)} + \mathbf{e}_{(j_x-2,j_y)} + \mathbf{e}_{(j_x,j_y+2)}\\
&+ \mathbf{e}_{(j_x,j_y-2)} + \mathbf{e}_{(j_x+1,j_y+1)}. \qquad (20)\end{aligned}$$

where in the additional cluster we have included now all members of the second-neighbour shell, assuming that their rotional jumps are in phase with those of the central molecule, *i.e.* in opposite phase with all the members of the first-neighbour shell. This leads to Lorentzians with a width parameter $\frac{1}{\tau_1}\lambda_{\mathbf{k}}^{(1)} + \frac{1}{\tau_2}\lambda_{\mathbf{k}}^{(2)}$, where $\lambda_{\mathbf{k}}^{(1)}$ is given by equation (15), while $\lambda_{\mathbf{k}}^{(2)} = -2\ell^2 + 2\sum_{(j_x,j_y)\in\mathcal{L}}\cos\left[\frac{2\pi}{n}\left(k_{(j_x,j_y)} - k_{(j_x+1,j_y)} - k_{(j_x-1,j_y)} - k_{(j_x,j_y+1)} - k_{(j_x,j_y-1)} + k_{(j_x-1,j_y+1)} + k_{(j_x+1,j_y-1)} + k_{(j_x+2,j_y)} + k_{(j_x-1,j_y-1)} + k_{(j_x-2,j_y)} + k_{(j_x,j_y+2)} + k_{(j_x,j_y-2)} + k_{(j_x+1,j_y+1)} - 5\right)\right]$. We can appreciate that in general the width parameter for the Lorentzian $L_{\mathbf{k}}$ will be

$$\sum_{r=1}^{\rho}\frac{1}{\tau_r}\left(-2N + 2\sum_{\mathbf{j}\in\mathcal{L}}\cos\left[\frac{2\pi}{n}\mathcal{P}_{\mathbf{j},r}\right]\right), \qquad (21)$$

since each cluster, *i.e.* each term $\mathbf{v}_{\mathbf{j},r}$ introduces a term $-2N + 2\sum_{\mathbf{j}\in\mathcal{L}}\cos(2\pi\mathcal{P}_{\mathbf{j},r}/n)$, where the polynomial $\mathcal{P}_{\mathbf{j},r}$ in the $k$'s is obtained by replacing each symbol $\mathbf{e}$ by a symbol $k$ in the definition of $\mathbf{v}_{\mathbf{j},r}$ and adding $-\mathbf{k}_0\cdot\mathbf{v}_{\mathbf{j},r}$. After combining with $\delta_{1k_{(1,1)}}\delta_{1k_{(1,2)}}\ldots\delta_{1k_{(j_x,j_y-1)}}\delta_{1k_{(j_x,j_y+1)}}\ldots\delta_{1k_{(\ell,\ell-1)}}\delta_{1k_{(\ell,\ell)}}$ in the example of equation (20) we recover $-4(\frac{5}{\tau_1} + \frac{13}{\tau_2})\sin^2[\frac{\pi}{n}(k-1)]$ provided $\mathcal{S} = \mathcal{H}$. (Here we have used the fact that the set of values $k_{(j_x,j_y)}\in\mathbb{Z}/n$ is the same for all molecules $(j_x,j_y)$, such that identical values coming from different values of $(j_x,j_y)$ can be regrouped in a term where the $k$-value is simply noted as $k$). The more different types of clusters one includes, the more likely the configuration space $\mathcal{S}$ will cover the whole of $\mathcal{H}$. In fact, if also single-molecule jumps are allowed we forcedly end up with $\mathcal{S} = \mathcal{H}$. Also for the final expression of the Lorentzian widths after the application of the selection rules it is not difficult to derive the general result: $-4\left[\sum_{r=1}^{\rho}(m_r/\tau_r)\right]\sin^2[\frac{\pi}{n}(k-1)]$, where $m_r$ is the number of molecules involved in cluster $r$. The use of the quantity $m_r$ exploits the fact that in general the correlations between the molecules will be symmetrical. The most striking point is that all this follows almost effortless, even for very complex situations, as the translational invariance on $\mathcal{H}$ establishes a kind of dictionary $\mathbf{v}_{\mathbf{j},r}\to\mathcal{P}_{\mathbf{j},r}$ which allows immediately to write down the eigenvalues, and that these eigenvalues are further tremendously simplified by the selection rule for the $\mathbf{k}$-values.

## 8 Conclusion

We conclude: Apart from a possible renormalization of the jump time, the signal in presence of correlations of the type we considered is the same as in total absence of correlations. In other words: Coherent quasielastic neutron scattering is unable to reveal possible correlations of the type we considered between the rotational jumps of the molecules. This is a clear, but non-trivial result. We may call it paradoxical that coherent scattering cannot reveal the type of correlations we considered, while incoherent scattering can. The finding that the widths are renormalized calls for caution in the interpretation of such widths in the results of an experiment. One would be inclined to interpret them as simple quantities corresponding to the relaxation of a single molecule, while their real meaning could be quite different. That is another important result of our work.

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37. $\mathbb{Z}/n = [1, n] \cap \mathbb{N}$ is the set of integers (or residue classes) *modulo n*
38. The configuration space is not a vector space, as the number set used will most of the time be of the type $\mathbb{Z}/n$, which is not a number field. In a genuine vector space we cannot have $(\,\exists\lambda \neq 0\,)\,(\,\exists\mathbf{v} \neq \mathbf{0}\,)\,\lambda\mathbf{v} \equiv \mathbf{0}$