Franck–Condon picture of incoherent neutron scattering

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A spectroscopic interpretation of incoherent neutron scattering experiments is presented which is based on Franck–Condon-type probabilities for scattering-induced transitions between quantum states of the target. The resulting expressions for the scattering functions enable an energy landscape-oriented analysis of neutron scattering spectra as well as a physical interpretation of Van Hove's space–time correlation functions in the quantum regime that accounts for the scattering kinematics. They suggest moreover a combined analysis of quasi- and inelastic scattering that becomes inseparable for complex systems with slow power-law relaxation.

neutron scattering theory | quasielastic neutron scattering | energy landscapes | complex systems | Van Hove theory

Incoherent thermal neutron scattering is an established technique for studying the average single-atom dynamics in molecular systems. As far as the stochastic, diffusive dynamics is concerned, one usually speaks of quasielastic neutron scattering (QENS) (1–3). The accessible time scales for QENS experiments are roughly between 0.001 and 100 ns and the accessible length scales between 1 and 100 Å. QENS is in particular increasingly used to study the internal dynamics of complex molecular systems, such as proteins, which is characterized by self-similarity. Such a behavior can be qualitatively explained by viewing the dynamics of the target system as a thermally activated hopping process between the many energetically almost equivalent minima ("conformational substates") of a fractal free energy landscape (FEL). This idea has been introduced by Frauenfelder (4) in the context of protein dynamics, but the concept applies to any complex physical system with a broad spectrum of (free) energy levels. It is, however, not a trivial task to integrate the FEL picture into a quantitative analysis of neutron scattering experiments. In a series of recent papers, Frauenfelder, Fenimore, and Young proposed a corresponding approach ("energy landscape model"), which is inspired by Mößbauer spectroscopy (5–7). The widely used analysis of QENS in terms of "spatial motion models" (3, 8, 9), which is based on Van Hove's theory of neutron scattering (10), is claimed to give the wrong picture of QENS. This has led to controversial discussions (11, 12), and here only a few remarks are added that are meant to motivate the approach to modeling QENS and incoherent neutron scattering in general that will be presented in this paper. In the energy landscape model by Frauenfelder and coworkers, the effects of momentum and energy transfer are essentially treated in the framework of classical mechanics, using physically plausible arguments for proteins but not a systematic approach on the basis of quantum mechanical scattering theory. The criticized classical QENS models are identified with the underlying neutron scattering theory developed by Van Hove (10), overlooking, however, that nothing is wrong with his space–time interpretation of neutron scattering experiments, as long as one does not consider the classical limit "$\hbar \to 0$" of the scattering functions. In this limit, which is indeed used in most QENS models, not only are quantum properties of the scattering system disregarded but so is the scattering kinematics—that is, the local perturbation of the sample by the incident neutrons (13, 14). The corresponding classical scattering functions do not fulfill the detailed balance symmetry relation of quantum time correlation

functions, which is reflected in QENS spectra from molecular systems if the energy transfer becomes a noticeable fraction of the thermal energy, $k_B T$. In Frauenfelder's QENS model, the perturbation of the sample by the scattered neutrons is represented in the form of a transient local pressure the incident neutron exerts on the environment of the scattering atom, but the scattering kinematics is not completely accounted for, since momentum and energy change of the scattered neutrons are not connected and energy changes just are Doppler-type passive recordings of the scattering system's "hops" on the FEL.

The idea of this paper is to develop a spectroscopic analysis of incoherent neutron scattering experiments on the basis of quantum mechanical scattering theory, which fully integrates the scattering kinematics and facilitates the interpretation of neutron scattering spectra from complex systems within the energy landscape picture. The paper attempts moreover to give a new physical interpretation of Van Hove's space–time correlation functions in the quantum case and to establish a physically intuitive relation to their classical counterparts.

Wick's Interpretation of Plane Wave Neutron Scattering

In 1954, when Van Hove (10) presented his famous paper on neutron scattering theory, Gian-Carlo Wick (15) presented a completely different but equivalent form, which is the starting point for the description of neutron scattering experiments presented in this paper. Similar to Van Hove, Wick starts from standard scattering theory, where neutron scattering experiments are described within the Born approximation, using the Fermi pseudopotential to model the short-ranged interactions between the neutron and the atomic nuclei in the sample under consideration (2). The incident neutrons are described by plane waves, with a well-defined initial momentum, $\mathbf{p}_0 = \hbar \mathbf{k}_0$, and leave the sample again with a well-defined momentum $\mathbf{p} = \hbar \mathbf{k}$. In this case, the differential scattering cross-section per atom is given by the relation

Significance

Despite the long history of neutron scattering studies on complex condensed matter systems, there is still a need for appropriate analysis concepts beyond the classical Van Hove theory, which is commonly used to interpret the experimental spectra in terms of trajectory-based dynamical models. The approach presented in this paper, which is based on quantum mechanical transition rather than on classical displacement probabilities, accounts by construction for the scattering kinematics and opens perspectives for the interpretation of quasielastic neutron scattering experiments from complex systems.

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$$\frac{d^2\sigma}{d\Omega d\omega} = \frac{|\mathbf{k}|}{|\mathbf{k}_0|}\mathcal{S}(\mathbf{q},\omega), \qquad \textbf{[1]}$$

where $\mathcal{S}(\mathbf{q},\omega)$ is the dynamic structure factor that carries the information about the microscopic structure and dynamics of the system under consideration. The variables $\mathbf{q} = (\mathbf{p}_0 - \mathbf{p})/\hbar$ and $\omega = (E_0 - E)/\hbar$ denote, respectively, the momentum and energy transfer from the neutron to the sample in units of $\hbar$. Considering samples like polymers and biopolymers, which contain a large amount of predominantly incoherently scattering hydrogen atoms, it follows that $\mathcal{S}(\mathbf{q},\omega) \approx |b_{H,inc}|^2 S_s(\mathbf{q},\omega)$, where $b_{H,inc}$ is the incoherent scattering length of hydrogen and $S_s(\mathbf{q},\omega)$ describes the particle-averaged dynamics of the hydrogen atoms in the sample:

$$S_s(\mathbf{q},\omega) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} dt\, e^{-i\omega t} F_s(\mathbf{q},t), \qquad \textbf{[2]}$$

$$F_s(\mathbf{q},t) = \frac{1}{N}\sum_{\alpha\in H}\left\langle e^{-i\mathbf{q}\cdot\hat{\mathbf{r}}_\alpha(0)}e^{i\mathbf{q}\cdot\hat{\mathbf{r}}_\alpha(t)}\right\rangle. \qquad \textbf{[3]}$$

$F_s(\mathbf{q},t)$ is referred to as intermediate scattering function and $\hat{\mathbf{r}}_\alpha$ is the position operator of hydrogen atom α in the sample. The symbol $\langle\ldots\rangle$ denotes here a quantum ensemble average, and the intermediate scattering function is a quantum time correlation function. The index "s" indicates that self-correlations in dynamics of the hydrogen atoms are probed.

Wick uses now the fact that position operators are generators for translations in momentum space and transforms expression (3) into

$$F_s(\mathbf{q},t) = \frac{1}{N}\sum_{\alpha\in H}\left\langle e^{it\hat{H}_\alpha(\mathbf{q})/\hbar}e^{-it\hat{H}/\hbar}\right\rangle, \qquad \textbf{[4]}$$

where $\hat{H}$ is the Hamilton operator of the sample and $\hat{H}_\alpha(\mathbf{q})$ is obtained by shifting the momentum of atom α by $\hbar\mathbf{q}$:

$$\hat{H} = \sum_{\mu=1}^{N}\frac{\hat{\mathbf{p}}_\mu^2}{2M_\mu} + V(\hat{\mathbf{r}}_1,\ldots,\hat{\mathbf{r}}_N), \qquad \textbf{[5]}$$

$$\hat{H}_\alpha(\mathbf{q}) = \sum_{\mu=1}^{N}\frac{(\hat{\mathbf{p}}_\mu + \delta_{\alpha\mu}\hbar\mathbf{q})^2}{2M_\mu} + V(\hat{\mathbf{r}}_1,\ldots,\hat{\mathbf{r}}_N). \qquad \textbf{[6]}$$

Here M_μ is the mass of hydrogen atom μ and $\hat{\mathbf{p}}_\mu$ is its momentum operator. The Hamilton operator $\hat{H}_\alpha(\mathbf{q})$ carries thus the "kick," which atom α receives from the scattered neutron.

A Franck–Condon Picture of Neutron Scattering

Discrete Energy Spectra. We consider first the situation that the eigenvalue spectrum of the Hamiltonian describing the dynamics of the scattering system is discrete, such that $\hat{H}|\phi_n\rangle = E_n|\phi_n\rangle$. The eigenstates $|\phi_n\rangle$ of $\hat{H}$ are supposed to form an orthonormal basis in a corresponding Hilbert space. For simplicity, we make the second assumption that all hydrogen atoms are physically equivalent, such that

$$F_s(\mathbf{q},t) = \left\langle e^{it\hat{H}'(\mathbf{q})/\hbar}e^{-it\hat{H}/\hbar}\right\rangle \quad \text{where} \quad \hat{H}' \equiv \hat{H}_1 \qquad \textbf{[7]}$$

and atom 1 is the arbitrarily chosen scattering atom. The eigenstates of the perturbed Hamiltonian, $\hat{H}'(\mathbf{q})$, here denoted as $|\phi_n'(\mathbf{q})\rangle$, constitute another orthonormal basis, and it follows from the completeness of the two bases that the intermediate scattering function can be formally expressed as

$$F_s(\mathbf{q},t) = \frac{1}{Z}\sum_{m,n} e^{-\beta E_m} e^{i(E_n' - E_m)/\hbar}|a_{m\to n}(\mathbf{q})|^2, \qquad \textbf{[8]}$$

where $a_{m\to n}(\mathbf{q}) = \langle\phi_n'(\mathbf{q})|\phi_m\rangle$ are the projections of the unperturbed eigenstates onto the perturbed ones. Here, $Z =$

$\sum_m e^{-\beta E_m}$ is the partition function of the scattering system, where $\beta = 1/(k_B T)$ with k_B being the Boltzmann constant and T the temperature in Kelvin.

The transition amplitudes $a_{m\to n}(\mathbf{q})$ take a particularly simple form if one works in momentum space representation, where momentum operators are replaced by normal vectors, $\hat{\mathbf{p}}_\alpha \to \mathbf{p}_\alpha$, and position operators by differential operators, $\hat{\mathbf{r}}_\alpha \to i\hbar\partial/\partial\mathbf{p}_\alpha$. One sees immediately that the eigenfunctions corresponding to the shifted Hamiltonian have the same functional form as those of the original one. Defining $\tilde{\phi}_m(\mathbf{P}) \equiv \langle\mathbf{P}|\phi_m\rangle$ to be the eigenfunctions of the unperturbed Hamiltonian in momentum space, we have

$$\hat{H}\tilde{\phi}_n(\mathbf{P}) = E_n\tilde{\phi}_n(\mathbf{P}), \qquad \textbf{[9]}$$

$$\hat{H}'(\mathbf{q})\tilde{\phi}_n(\mathbf{P}+\hbar\mathbf{Q}) = E_n\tilde{\phi}_n(\mathbf{P}+\hbar\mathbf{Q}). \qquad \textbf{[10]}$$

We note that

$$\tilde{\phi}_m(\mathbf{P}) = \frac{1}{(2\pi\hbar)^{3N/2}}\int d^{3N}R\, e^{-i\mathbf{R}\cdot\mathbf{P}/\hbar}\phi_m(\mathbf{R}),$$

$$\phi_m(\mathbf{R}) = \frac{1}{(2\pi\hbar)^{3N/2}}\int d^{3N}P\, e^{i\mathbf{R}\cdot\mathbf{P}/\hbar}\tilde{\phi}_m(\mathbf{P}),$$

where $\phi_m(\mathbf{R}) = \langle\mathbf{R}|\phi_m\rangle$ is the wave function in position space. Here and in the following, the vectors $\mathbf{R}$ and $\mathbf{P}$ comprise the $3N$ components of all N atomic positions and momenta, respectively, and the components of $\mathbf{Q}$ are defined such that the operation $\mathbf{P}+\hbar\mathbf{Q}$ shifts only the momentum of the scattering atom—that is, $Q_1 = q_x$, $Q_2 = q_y$, $Q_3 = q_z$, and $Q_j = 0$ for $3 < j \le 3N$. It follows then from Eq. 10 that $\tilde{\phi}_n'(\mathbf{P};\mathbf{q}) = \tilde{\phi}_n(\mathbf{P}+\hbar\mathbf{Q})$ and that $E_n' = E_n$, such that the coefficient $a_{m\to n}(\mathbf{q})$ can be expressed as overlap integrals involving the shifted and unshifted energy eigenfunctions of the unperturbed Hamiltonian in momentum space,

$$a_{m\to n}(\mathbf{q}) = \int d^{3N}p\, \tilde{\phi}_n^*(\mathbf{P}+\hbar\mathbf{Q})\tilde{\phi}_m(\mathbf{P}). \qquad \textbf{[11]}$$

The squared transition amplitudes,

$$w_{m\to n}(\mathbf{q}) \equiv |a_{m\to n}(\mathbf{q})|^2, \qquad \textbf{[12]}$$

fulfill the relations

$$\sum_m w_{m\to n}(\mathbf{q}) = \sum_n w_{m\to n}(\mathbf{q}) = 1, \qquad \textbf{[13]}$$

$$w_{m\to n}(\mathbf{0}) = \delta_{mn}, \qquad \textbf{[14]}$$

and can be interpreted as probabilities for the neutron scattering-induced transitions $|\phi_m\rangle \to |\phi_n\rangle$ for a given momentum transfer $\hbar\mathbf{q}$. Using the notation Eq. **12**, the intermediate scattering function and the corresponding dynamic structure factor take the form

$$F_s(\mathbf{q},t) = \frac{1}{Z}\sum_{m,n} e^{-\beta E_m} e^{it(E_n - E_m)/\hbar} w_{m\to n}(\mathbf{q}), \qquad \textbf{[15]}$$

$$S_s(\mathbf{q},\omega) = \frac{1}{Z}\sum_{m,n} e^{-\beta E_m} w_{m\to n}(\mathbf{q})\delta(\omega - [E_n - E_m]/\hbar). \qquad \textbf{[16]}$$

The symmetry property

$$w_{m\to n}(\mathbf{q}) = w_{n\to m}(-\mathbf{q}) \qquad \textbf{[17]}$$

leads to the detailed balance relations

$$F_s(\mathbf{q}, t) = F_s(-\mathbf{q}, -t + i\beta\hbar), \qquad \textbf{[18]}$$

$$S_s(\mathbf{q}, \omega) = e^{\beta\hbar\omega} S_s(-\mathbf{q}, -\omega), \qquad \textbf{[19]}$$

which express that energy loss of the scattered neutrons is more likely than energy gain (2).

The Dirac distributions in the double sum (Eq. **16**) express that the total energy for the scattering system and the neutron is conserved, and Fig. 1 shows a sketch of the corresponding line spectrum. Each Dirac distribution is here slightly broadened to make it visible, and the broadening may be interpreted as the result of finite instrumental resolution. Splitting the double sum in Eq. **16** into terms with $m \neq n$ and $m = n$, one obtains a decomposition into, respectively, the inelastic and the elastic component of the spectrum. The latter is usually written as

$$S_s^{(\mathrm{el})}(\mathbf{q}, \omega) = EISF(\mathbf{q})\delta(\omega), \qquad \textbf{[20]}$$

where

$$EISF(\mathbf{q}) = \frac{1}{Z}\sum_m e^{-\beta E_m} w_{m\to m}(\mathbf{q}) \qquad \textbf{[21]}$$

is the Elastic Incoherent Structure Factor (EISF). It is the thermally weighted probability for the scattering system to stay in its initial energy level after the scattering of a neutron with momentum transfer $\hbar\mathbf{q}$.

The construction of the transition probabilities reminds the Franck–Condon theory of vibronic transitions in molecules (16, 17). In the latter case, one considers, however, overlap integrals of energy eigenfunctions in position space that correspond, respectively, to the molecular vibrational spectra before and after the absorption or emission of a photon. The absorption/emission of the photon changes the potential energy of the molecule, and this change entails a shift of its minimum in space (i.e., a shift of the atomic equilibrium configuration). In the case of neutron scattering, it is instead the kinetic energy of the atomic nuclei in the sample that is shifted due to the momentum transfer $\hbar\mathbf{q}$ of the neutron (see Fig. 2).

Continuous Energy Spectra. If the Hamiltonian of the scattering system has a continuous energy spectrum, the corresponding eigenvalue problem has the form

$$\hat{H}|\phi(X)\rangle = E(X)|\phi(X)\rangle, \qquad \textbf{[22]}$$

where the energy eigenstates, $|\phi(X)\rangle$, are described by a set of real-valued variables, $X \equiv \{x_1, \ldots, x_f\}$, and $E(X)$ is the energy
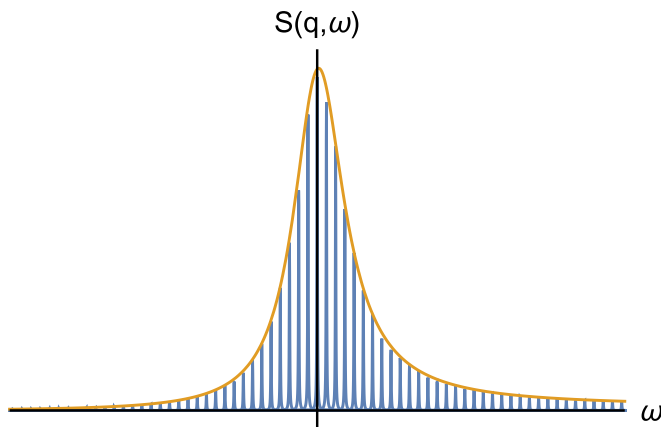

Fig. 2. Neutron scattering in the Franck–Condon representation. The model system is here the harmonic oscillator, and one considers the $0 \to 3$ excitation. T and T' are the kinetic energies, respectively, before and after the collision with the neutron and $T'(p) = T(p + \hbar q)$.

in these variables. We further assume that the eigenstates are normalized, such that

$$\langle\phi(X')|\phi(X)\rangle = \begin{cases} 1 & \text{if } X = X', \\ 0 & \text{otherwise.} \end{cases} \qquad \textbf{[23]}$$

The quantum states are counted via an appropriate density of states, $\rho(X)$, such that $m \to dm = \rho(X)d^f X$ and so forth, and it is convenient to work with probability densities instead of probabilities. The transition probability density is in particular defined as

$$W(X'|X; \mathbf{q}) = \rho(X')|a(X'|X; \mathbf{q})|^2, \qquad \textbf{[24]}$$

with

$$a(X'|X; \mathbf{q}) = \int d^{3N}p\, \tilde{\phi}^*(\mathbf{P} + \hbar\mathbf{Q}; X')\tilde{\phi}(\mathbf{P}; X) \qquad \textbf{[25]}$$

and $\tilde{\phi}(\mathbf{P}; X) \equiv \langle\mathbf{P}|\phi(X)\rangle$, and it fulfills the condition

$$W(X'|X, \mathbf{0}) = \delta(X - X'). \qquad \textbf{[26]}$$

Similarly, we define the equilibrium probability density

$$W_{\mathrm{eq}}(X) = \rho(X)\frac{e^{-\beta E(X)}}{Z}, \qquad \textbf{[27]}$$

where $Z = \int d^f X\, \rho(X)\exp(-\beta E(X))$. With these prerequisites, the intermediate scattering function takes the form

$$F_s(\mathbf{q}, t) = \int\int d^f X d^f X'\, W_{\mathrm{eq}}(X)$$
$$\times e^{i(E(X') - E(X))t/\hbar} W(X'|X; \mathbf{q}), \qquad \textbf{[28]}$$

and the resulting dynamic structure factor reads

$$S_s(\mathbf{q}, \omega) = \int\int d^f X d^f X'\, W_{\mathrm{eq}}(X) W(X'|X; \mathbf{q})$$
$$\times \delta(\omega - [E(X') - E(X)]/\hbar), \qquad \textbf{[29]}$$

in analogy with Eq. **16**.

S(q,ω)

Fig. 1. Sketch of a Franck–Condon-type line spectrum for neutron scattering. The slight asymmetry is due to the detailed balance relation (Eq. **19**).
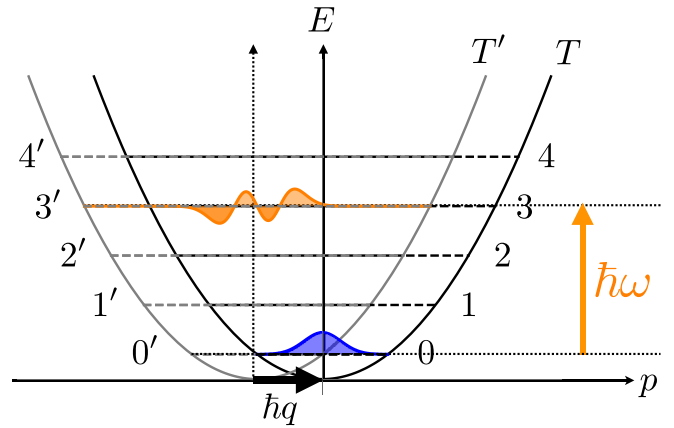
Illustrations for Two Model Systems

Quantum Oscillator. The harmonic oscillator is a simple quantum system with a discrete energy spectrum for which an analytical solution for the Franck–Condon-type transition probabilities and the resulting scattering functions can be found. The potential energy function is here a quadratic function of the displacement coordinate, x,

$$V(x) = \frac{1}{2} M \Omega^2 x^2,$$

and the corresponding eigenvalue spectrum of the Hamiltonian is equidistant, $E_n = (n + 1/2)\hbar\Omega$. Introducing the dimensionless momentum transfer

$$y(q) = \sqrt{\frac{2\hbar}{M\Omega}} q, \qquad \textbf{[30]}$$

the transition probabilities can be computed analytically from the well-known oscillator eigenfunctions, which have the same form in position and momentum space, and the result is found to be (see *SI Appendix*)

$$w_{m \to n}(q) = e^{-\frac{y^2}{4}} (-1)^{m+n} L_m^{(n-m)}\left(\frac{y^2}{4}\right) L_n^{(m-n)}\left(\frac{y^2}{4}\right), \quad \textbf{[31]}$$

where $L_m^{(\alpha)}(.)$ denote the generalized Laguerre polynomials (18). A few examples are given in Fig. 3. Due to the symmetry of the potential, they depend only on the absolute value of the momentum transfer and not on its sign. The intermediate scattering function can be written in the equivalent forms (see *SI Appendix*)

$$F_s(q, t) = \frac{1}{Z} \sum_{m,n} e^{-\beta\hbar\Omega(m+1/2)} e^{i(n-m)\Omega t} w_{m\to n}(y(q)), \quad \textbf{[32]}$$

$$= e^{i\frac{y(q)^2}{4}\left(\sin(\Omega t) + i(1-\cos(\Omega t))\coth\left(\frac{\beta\Omega\hbar}{2}\right)\right)}, \quad \textbf{[33]}$$

where the partition function is given by $Z = e^{\frac{1}{2}\beta\hbar\Omega}/(e^{\beta\hbar\Omega} - 1)$, and Eq. **33** is equivalent with the formula stated in the classical textbook by Lovesey (2). The corresponding expressions for the dynamic structure factor are
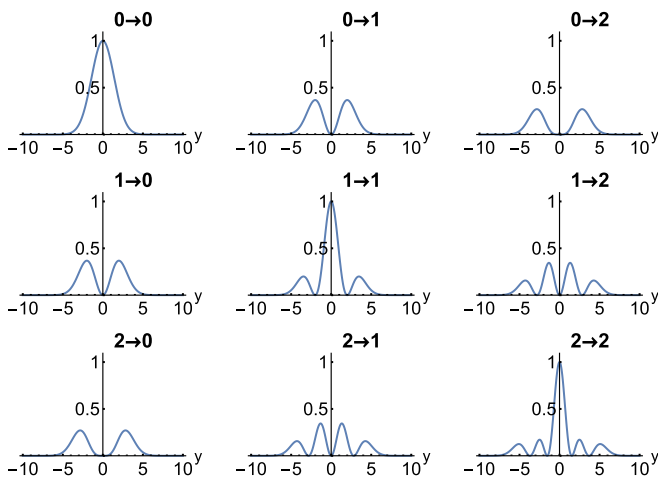
Fig. 3. Probabilities $w_{m\to n}(y)$ for the transition $m \to n$ of the harmonic oscillator. The variable y is the dimensionless momentum transfer defined by Eq. **30**.

$$S_s(q, \omega) = \frac{1}{Z} \sum_{m,n} e^{-\beta\hbar\Omega(m+1/2)} \delta(\omega - [n-m]\Omega) w_{m\to n}(q), \tag*{[34]}$$

$$= e^{-\frac{y(q)^2}{4}\coth\left(\frac{\beta\hbar\Omega}{2}\right) + \frac{\beta\hbar\omega}{2}} \sum_{n=-\infty}^{+\infty} I_n(a(q))\delta(\omega - n\Omega), \tag*{[35]}$$

with $I_n(.)$ being the Bessel functions and $a(q) = y(q)^2/(4\sinh(\beta\hbar\Omega/2))$.

Ideal Gas. The ideal gas is the simplest model for a system with a continuous distribution of quantum states. Between collisions, individual molecules move freely, without the influence of forces. The quantum state of a freely moving particle is characterized by the three components of its sharply defined momentum, $\mathbf{p}_0$—that is, $X = \{p_{0,x}, p_{0,y}, p_{0,z}\}$. The corresponding wave functions in position space are 3D-plane waves, $\langle\mathbf{r}|\phi(\mathbf{p}_0)\rangle \propto \exp(i\mathbf{p}_0 \cdot \mathbf{r}/\hbar)$, and lead to a momentum representation of the form $\langle\mathbf{p}|\phi(\mathbf{p}_0)\rangle = \delta(\mathbf{p} - \mathbf{p}_0)$. Since these wave functions are not square-normalizable, the state of the scattering atom is described by a square-normalized Gaussian wave packet, which is sharply peaked around $\mathbf{p} = \mathbf{p}_0$,

$$\tilde{\phi}(\mathbf{p}; \mathbf{p}_0) = \frac{1}{(2\pi\epsilon^2)^{3/4}} e^{-\frac{(\mathbf{p}-\mathbf{p}_0)^2}{4\epsilon^2}}, \qquad \textbf{[36]}$$

where $\tilde{\phi}(\mathbf{p}; \mathbf{p}_0) \equiv \langle\mathbf{p}|\phi(\mathbf{p}_0)\rangle$. Setting $\rho(\mathbf{p}_1) = 1/(2\sqrt{\pi}\epsilon)^3$ for the density of final states labeled by $\mathbf{p}_1$, the resulting transition probability has the form (see *SI Appendix*)

$$W(\mathbf{p}_1|\mathbf{p}_0; \mathbf{q}) = \frac{e^{-\frac{(\mathbf{p}_0 - \mathbf{p}_1 + \hbar\mathbf{q})^2}{4\epsilon^2}}}{(2\sqrt{\pi}\epsilon)^3} \overset{\epsilon\to 0}{=} \delta(\mathbf{p}_0 + \hbar\mathbf{q} - \mathbf{p}_1) \qquad \textbf{[37]}$$

and expresses strict momentum conservation in the limit $\epsilon \to 0$. Inserting the right-hand side together with the Maxwell equilibrium distribution, $W_{eq}(\mathbf{p}_0) = (2\pi M/\beta)^{-3/2} \exp(-\beta\mathbf{p}_0^2/2M)$, into the general Eq. **28** for the intermediate scattering function, one is left with a simple volume integral over $\mathbf{p}_0$, which can be easily computed and yields the well-known form for the intermediate scattering function of an ideal gas consisting of molecules with mass M (2),

$$F_s(\mathbf{q}, t) = e^{-\frac{q^2 t(t-i\beta\hbar)}{2\beta M}}, \qquad \textbf{[38]}$$

where $q \equiv |\mathbf{q}|$ is the modulus of the momentum transfer. The corresponding dynamic structure factor also has a Gaussian form:

$$S_s(\mathbf{q}, \omega) = \left(\frac{2\pi q^2}{\beta M}\right)^{-1/2} e^{-\frac{\beta(\hbar q^2 - 2M\omega)^2}{8Mq^2}}. \qquad \textbf{[39]}$$

Reinterpreting the Van Hove Function

Van Hove introduced the spatial Fourier transform of the intermediate (self)-scattering function,

$$G_s(\mathbf{r}, t) = \frac{1}{(2\pi)^3} \int d^3q \, e^{-i\mathbf{q}\cdot\mathbf{r}} F_s(\mathbf{q}, t),$$

$$= \int d^3r' \langle\delta(\mathbf{r} - \mathbf{r}' + \hat{\mathbf{r}}_1(0))\delta(\mathbf{r}' - \hat{\mathbf{r}}_1(t))\rangle, \qquad \textbf{[40]}$$

to relate the $(\mathbf{r}, t)$-space of spatial motions to the $(\mathbf{q}, \omega)$-space of neutron scattering spectra:

$$S_s(\mathbf{q}, \omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt \int d^3r \, e^{i(\mathbf{q}\cdot\mathbf{r} - \omega t)} G_s(\mathbf{r}, t). \qquad \textbf{[41]}$$

The Van Hove function takes the convenient form of a probability density for displacements $\mathbf{r}$ within time t if one considers the classical approximation

$$G_s(\mathbf{r}, t) \approx \langle \delta(\mathbf{r} - [\mathbf{r}_1(t) - \mathbf{r}_1(0)]) \rangle_{\text{cl}}, \qquad [42]$$

which is the standard assumption in modeling QENS spectra. The index "cl" indicates a classical phase space ensemble average.

The spectroscopic picture of neutron scattering in this paper gives more insight into the physical meaning of the quantum Van Hove correlation function. If Eq. **15** for the intermediate scattering function is inserted into the definition (Eq. **40**) of the Van Hove (self)-correlation function, one obtains

$$G_s(\mathbf{r}, t) = \frac{1}{Z} \sum_{m,n} e^{-\beta E_m} e^{it(E_n - E_m)/\hbar} g_{m \to n}(\mathbf{r}), \qquad [43]$$

where the functions $g_{m \to n}(\mathbf{r})$ are the Fourier transforms of the transition probabilities,

$$g_{m \to n}(\mathbf{r}) = \frac{1}{(2\pi)^3} \int d^3 q \, e^{-i\mathbf{q}\cdot\mathbf{r}} w_{m \to n}(\mathbf{q}). \qquad [44]$$

For simplicity, we consider here only discrete energy spectra. Since $w_{m \to n}(\mathbf{q}) = |a_{m \to n}(\mathbf{q})|^2$, it follows from the correlation theorem of the Fourier transform that

$$g_{m \to n}(\mathbf{r}) = \int d^3 r' \, A_{m \to n}(\mathbf{r} + \mathbf{r}') A_{m \to n}^*(\mathbf{r}'), \qquad [45]$$

with $\quad A_{m \to n}(\mathbf{r}) = \frac{1}{(2\pi)^3} \int d^3 q \, e^{-i\mathbf{q}\cdot\mathbf{r}} a_{m \to n}(\mathbf{q}). \qquad [46]$

Noting that the transition amplitudes can be written as $a_{m \to n}(\mathbf{q}) = \int d^{3N} R \, e^{i\mathbf{Q}\cdot\mathbf{R}} \phi_n^*(\mathbf{R}) \phi_m(\mathbf{R})$, the functions $A_{m \to n}(\mathbf{r})$ can be expressed as partial overlap integrals

$$A_{m \to n}(\mathbf{r}) = \int d^3 r_2 \ldots d^3 r_N \, \phi_n^*(\mathbf{r}, \mathbf{r}_2, \ldots, \mathbf{r}_N) \phi_m(\mathbf{r}, \mathbf{r}_2, \ldots, \mathbf{r}_N) \qquad [47]$$

of the energy eigenfunctions $\phi_n(\mathbf{R})$ in position space. For $m = n$, we have in particular

$$A_{m \to m}(\mathbf{r}) = \int d^3 r_2 \ldots d^3 r_N \, |\phi_m(\mathbf{r}, \mathbf{r}_2, \ldots, \mathbf{r}_N)|^2 . \qquad [48]$$

This is the marginal probability density to find the scattering atom at position $\mathbf{r}$ for the case that the system is before and after the scattering process in the same energy eigenstate $|\phi_m\rangle$. For $m \neq n$, the Fourier transformed transition amplitudes $A_{n \to m}(\mathbf{r})$ cannot be considered as probability densities, since they are generally complex. They verify the symmetry relation $A_{m \to n}^*(\mathbf{r}) = A_{n \to m}(\mathbf{r})$, such that $g_{m \to n}^*(\mathbf{r}) = g_{n \to m}(\mathbf{r})$.

The time variable can be straightforwardly integrated into the formalism by introducing the time-dependent wave functions

$$\psi_m(\mathbf{R}, t) = \phi_m(\mathbf{R}) e^{-iE_m t/\hbar} \qquad [49]$$

and the corresponding time-dependent transition overlap integrals

$$T_{m \to n}(\mathbf{r}, t) = \int d^3 r_2 \ldots d^3 r_N \, \psi_n^*(\mathbf{r}, \mathbf{r}_2, \ldots, \mathbf{r}_N, t) \\ \times \psi_m(\mathbf{r}, \mathbf{r}_2, \ldots, \mathbf{r}_N, t). \qquad [50]$$

With these definitions, the Van Hove self-function is given by

$$G_s(\mathbf{r}, t) = \frac{1}{Z} \sum_{m,n} e^{-\beta E_m} G_{m \to n}(\mathbf{r}, t), \qquad [51]$$

and each coefficient

$$G_{m \to n}(\mathbf{r}, t) = \int d^3 r \, T_{m \to n}(\mathbf{r} + \mathbf{r}', t) T_{m \to n}^*(\mathbf{r}', 0) \qquad [52]$$

corresponds to the neutron scattering-induced energy transition $m \to n$.

In this context, it is instructive to come back to the classical limit of the Van Hove correlation function, which is defined by Eq. **42**. In this case,

$$G_{\Gamma(0) \to \Gamma(t)}^{(cl)}(\mathbf{r}, t) = \delta(\mathbf{r} - [\mathbf{r}_1(t) - \mathbf{r}_1(0)]) \qquad [53]$$

corresponds to the coefficient $G_{m \to n}(\mathbf{r}, t)$, where $\Gamma(0)$ is a point in phase space describing the state of the system at time $t = 0$ and $\Gamma(t)$ is the point in phase space to which the system evolves in time t. This final point is exactly determined by the laws of classical Hamiltonian mechanics, and one can formally write $\mathbf{r}(t) \equiv \mathbf{r}(\Gamma(t))$ and $\mathbf{r}(0) \equiv \mathbf{r}(\Gamma(0))$. Therefore, there is no integral over the final points in phase space, which would correspond to the sum over the energy levels n in the quantum case, and only the thermal average over the initial points in phase space is performed to compute $G^{(cl)}(\mathbf{r}, t)$. The fact that the phase space point $\Gamma(t)$ is entirely determined by $\Gamma(0)$ and t is equivalent to saying that the trajectory of the scattering atom is not deviated by the impact of the neutron. In the classical Van Hove theory, quantum transition probabilities are thus replaced by classical "transition certainties," and the masses of the scattering atoms are considered infinite as far as the scattering kinematics is concerned. Such a description is, for example, appropriate for neutron scattering from large molecules performing rigid body motions.

QENS from Complex Systems

We consider now QENS from complex systems, where the distribution of energy levels is quasi-continuous in the range of accessible energy transfers. In the case of macromolecules like proteins, we are looking in the first place at their internal dynamics, which is characterized by a vast spectrum of time scales and corresponding motion types. The physical model for neutron scattering is here a scattering atom that receives a momentum transfer $\hbar\mathbf{q}$ by the incoming neutrons and that transmits this kick to a macromolecular matrix with quantum mechanical degrees of freedom. Choosing the energy to specify the quantum state of the scattering system, the dynamic structure factor takes a particularly simple form. Setting $X \equiv E$ in Eq. **29**, the integral over $X' \equiv E'$ can be performed to yield

$$S_s(\mathbf{q}, \omega) = \hbar \int dE \, W_{\text{eq}}(E) \, W(E + \hbar\omega | E; \mathbf{q}). \qquad [54]$$

The incoherent dynamic structure factor thus becomes a thermally averaged probability density for energy transitions $E \to E + \hbar\omega$, which are induced by a momentum transfer $\mathbf{q}$.

The direct calculation of $S_s(\mathbf{q}, \omega)$ via Eq. **54** will in general not be possible, but the formula suggests that there is no a priori
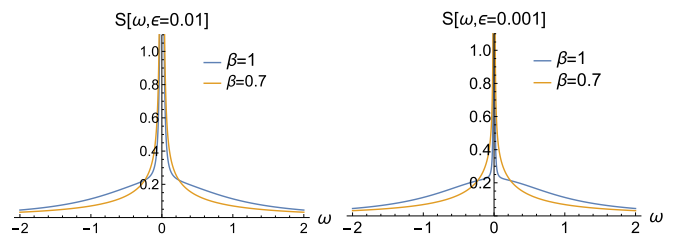
Fig. 4. (*Left*) Dynamic structure factor corresponding to the intermediate scattering function (Eq. **55**), with $R(t)$ given by Eq. **57**. Here $\tau = 1$, *EISF* = 0.3, and $\epsilon = 0.01$. (*Right*) The same figure for $\epsilon = 0.001$.

distinction between elastic ($\omega = 0$) and quasielastic scattering (ω in the vicinity of 0). This has also been suggested in ref. 6, and in the following, it will be shown that elastic and quasielastic scattering are practically not separable for complex systems with slow power-law relaxation. For this purpose, we consider an intermediate scattering function of the form (the q-dependence is dropped)

$$F_s(t) = EISF + (1 - EISF)R(t),\qquad\textbf{[55]}$$

where $0 < EISF < 1$ due to elastic scattering and $R(t)$ is a relaxation function fulfilling $R(0) = 1$ and $\lim_{t \to \infty} R(t) = 0$. The dynamic structure factor in the vicinity of $\omega = 0$ can then be obtained on the basis of purely mathematical arguments and is directly determined by the asymptotic form of the intermediate scattering function for long times (see *SI Appendix*),

$$S_s(\omega) \overset{\omega \to 0}{\sim} \lim_{\epsilon \to 0+} \frac{1}{\pi} \Re \left\{ \frac{F_s(1/(i\omega + \epsilon))}{i\omega + \epsilon} \right\}.\qquad\textbf{[56]}$$

The parameter $\epsilon > 0$ can be thought of as instrumental resolution. It follows from Eq. **56** that the ratio of quasielastic and elastic scattering at $\omega = 0$ is increasingly smaller for exponential than for power law relaxation, as ϵ tends to 0. This indicates that these components can be well separated in the first case and not well in the second. To investigate the separability of the elastic and quasielastic components of a neutron scattering spectrum for a concrete example, we consider a relaxation function of the form

$$R(t) = E_\beta(-(|t|/\tau)^\beta), \quad 0 < \beta \le 1,\qquad\textbf{[57]}$$

where $E_\beta(.)$ is the Mittag–Leffler function (18). With this definition, $R(t)$ smoothly interpolates between exponential relaxation ($\beta = 1$) and an asymptotic power-law decay if $|t| \gg \tau$ for $0 < \beta < 1$, where $R(t) \sim (t/\tau)^{-\beta}/\Gamma(1 - \beta)$ for $t \gg \tau$. Detailed balance effects are here neglected—that is, $\beta\hbar \ll \tau$. Fig. 4, *Left* shows a plot of the dynamic structure factors for $\beta = 1$ (blue line) and $\beta = 0.7$ (orange line), where in both cases $EISF = 0.3$, $\tau = 1$, and $\epsilon = 0.01$. For $\beta = 1$—that is, for exponential relaxation—one recognizes that the elastic peak is well separated from the broader quasielastic (Lorentzian) profile and that this distinction disappears for $\beta = 0.7$, where the decay is nonexponential. Fig. 4, *Right* displays the corresponding plot with a resolution $\epsilon = 0.001$ and shows that the nonseparability of elastic and quasielastic scattering persists with higher resolution for $\beta = 0.7$, while these components are even more clearly separated for $\beta = 1$. The nonseparability for $\beta = 0.7$ follows from the self-similarity of the dynamic structure factor for $\omega\tau \ll 1$, which is, in turn, a consequence of the power law decay of $R(t)$ for $t \gg \tau$. This illustration shows that elastic and quasielastic scattering from complex systems with slow power law relaxation cannot be separated in real-life experiments. Therefore, the EISF should here be part of a global model for both elastic and quasielastic scattering, either for a resolution-broadened dynamic structure factor or for the corresponding resolution-deconvolved intermediate scattering function.

A point of practical importance in this context is the treatment of the ω-asymmetry in QENS spectra, which is due to the detailed balance relation of quantum time correlation functions (this effect has not been considered in the above discussion). The results of a recent paper on a "model-free" description of neutron scattering from diffusing quantum particles (19) suggests that Schofield's semiclassical correction (20) $S_s(q, \omega) \propto \exp(\beta\hbar\omega/2)S_s^{(cl)}(q, \omega)$ or, equivalently, $F_s(q, t) \propto F_s^{(cl)}(q, t - i\beta\hbar/2)$ may be applied for modeling QENS experiments, using as input only the asymptotic form of the classical intermediate scattering function. The scattering functions must here be normalized to ensure the normalization condition $\int_{-\infty}^{+\infty} d\omega\, S_s(q, \omega) = 1 = F_s(q, 0)$, which is imposed by the probabilistic interpretation (Eq. **54**) of the dynamic structure factor.

Conclusions

In this paper, an interpretation of incoherent neutron scattering spectra has been presented in which probabilities for neutron scattering-induced transitions between different quantum states of the sample play a central role. The transition probabilities are expressed as squared Franck–Condon-type overlap integrals of corresponding eigenfunctions in momentum space, whose arguments are shifted by the momentum transfer from the neutron to the sample. A particular simple form of the dynamic structure factor is obtained if the quantum states are described by a (quasi)continuous set of energy eigenvalues. In this case, the dynamic structure factor is simply the thermally averaged transition probability density for energy transitions $E \to E + \hbar\omega$ and a momentum transfer $\hbar\mathbf{q}$. Corresponding consequences for the interpretation of QENS data have been discussed, in particular the smooth transition from elastic to quasielastic scattering for complex systems where the intermediate scattering function slowly decays with a power law. The elastic and quasielastic component of the scattering spectrum appear here as fused.

The theory connects Frauenfelder's idea of an energy landscape-based interpretation of neutron scattering experiments, in particular the decomposition of QENS spectra into "Mößbauer lines," with standard scattering theory. It provides moreover a physical interpretation for the complex quantum version of the Van Hove correlation functions and shows in particular that there exists a physical meaningful and intuitively understandable relation between the quantum and the classical version of the Van Hove functions.

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