

A Classical Approximation for the Neutron Scattering Dynamic Structure Factor

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1 Introduction

In an inelastic neutron scattering (INS) or inelastic X-ray scattering (IXS) experiment, the doubly-differential cross section basically tells us the probability that a particle in the incident beam is scattered in a particular direction with a particular change in energy. The doubly-differential cross section is proportional to the *dynamic structure factor* (DSF) $S(\mathbf{Q}, \omega)$ [1, 2]. The wave-vector \mathbf{Q} is the momentum transferred into the crystal and is directly related to the direction into which the incident particle scatters. $E = \hbar\omega$ is the energy transferred into the crystal by the particle. Neutron and X-ray scattering are the flag-ship methods for measuring atomic dynamics and structure in condensed matter, particularly for $\mathbf{Q} \neq 0$. We want to understand $S(\mathbf{Q}, \omega)$ in detail.

If we can calculate $S(\mathbf{Q}, \omega)$, we can directly model a scattering experiment. Usually we want to do this because we have measured the atomic dynamics in a crystal and found an interesting signal, but are having a hard time understanding what is going on. $S(\mathbf{Q}, \omega)$ is a thermal-average of the atomic dynamics [1], so deducing what is going on at the microscopic level is an inverse problem (i.e. it's hard). A successful method to attack the inverse problem is reverse Monte Carlo (RMC) [3]: we guess a configuration of the atoms and calculate the Boltzmann weight to deduce its likely hood. This is done for many configurations and they are averaged. If our guesses produce the right scattering intensity, then maybe we know what configurations produce the signal we care about. Still RMC is based on ensemble averaging, so we can really only probe the static microscopic structure: e.g. diffuse and Bragg scattering. This is analogous to the situation in Monte Carlo atomic simulation methods where we lose information about the *dynamics* that lead to a physical observable by averaging over configurations on different phase-space trajectories. If knowing the dynamics is important, one often uses *molecular dynamics* (MD) simulations instead [4]. So we need to know how to calculate $S(\mathbf{Q}, \omega)$ from MD. See ref. [5] for related information.

2 The Dynamic Structure Factor from Molecular Dynamics

We derive the equation used to calculate the DSF $S(\mathbf{Q}, \omega)$, from molecular dynamics here. The DSF is defined as [1]

$$\begin{aligned} S(\mathbf{Q}, \omega) &= \int \langle \hat{\rho}(\mathbf{r}, t) \hat{\rho}(0, 0) \rangle \exp(i(\mathbf{Q} \cdot \mathbf{r} - \omega t)) d\mathbf{r} dt \\ &\equiv \int G(\mathbf{r}, t) \exp(i(\mathbf{Q} \cdot \mathbf{r} - \omega t)) d\mathbf{r} dt \\ &\equiv \int F(\mathbf{Q}, t) \exp(-i\omega t) dt \end{aligned} \quad (1)$$

eq. 1 is the time- and space-Fourier transform of the density-density correlation function (also called the *Van Hove* function [6]), $G(\mathbf{r}, t)$. $\hat{\rho}(\mathbf{r}, t)$ is the quantum mechanical density operator: in first quantization, it is a function of the position operators $\hat{\mathbf{r}}(t)$.

Positions do not commute at different times t, t' so evaluating eq. 1 is difficult. To simplify the notation, we do not write the explicit time dependence of $\hat{\mathbf{r}}$ except where it is needed. The usual method to evaluate eq. 1 for crystals is to expand the position operators, $\hat{\mathbf{r}}$, in terms of the phonon creation and annihilation operators [2]. This works well when the harmonic approximation is sufficient, but at high-temperatures and particularly in molecular crystals where molecules rotate almost freely, this won't work. Instead, we approximate the positions as classical coordinates so that $\hat{\rho} \equiv \rho$ is classical and the classical positions $\mathbf{r}(t)$ can be determined using molecular dynamics simulations¹. Importantly we have made no assumptions about the configuration of the material, so this method is valid for liquids, disordered compounds, molecular crystals, etc. The main source of error in the classical approximation is that the scattering function $S(\mathbf{Q}, \omega)$ does not satisfy the principle of detailed balance [1, 2, 7]. It is possible to add corrections that include quantum mechanical effects [7]; however, I do not pursue this here. The classical approximation becomes valid at high-temperature where quantum effects on nuclear motion are negligible and the particles follow Maxwell-Boltzmann statistics.

For classical (i.e. commuting) positions, eq. 1 can be simplified. With

$$\delta(\mathbf{r} - \mathbf{r}_i) = \int \exp(-i\mathbf{Q} \cdot (\mathbf{r} - \mathbf{r}_i)) \frac{d\mathbf{Q}}{(2\pi)^3} \quad (2)$$

we can write $\rho(\mathbf{r}, t)$ as [1]

$$\rho(\mathbf{r}, t) = \sum_i^N b_i \int \exp(-i\mathbf{Q} \cdot (\mathbf{r} - \mathbf{r}_i)) \frac{d\mathbf{Q}}{(2\pi)^3}. \quad (3)$$

In eq. 3, b_i are the neutron scattering lengths. They are different for different types of atoms. i labels the atoms: it runs over all of the atoms in the simulation cell. The classical

¹ I believe that this can be shown to be a *stationary phase approximation* to the many-body correlation function in eq. 1... I am working on showing this in a different document.

expression for the Van Hove function, $G(\mathbf{r}, t)$ in eq. 1, is

$$G(\mathbf{r}, t) = \langle \rho(\mathbf{r}, t) \rho(0, 0) \rangle = \int \rho(\mathbf{r} + \mathbf{r}', t + t') \rho(\mathbf{r}', t') d\mathbf{r}' dt'. \quad (4)$$

Inserting eq. 3 into eq. 4 and carrying out the integrals, we find

$$G(\mathbf{r}, t) = \sum_i^N \sum_j^N b_i b_j \int \delta(\mathbf{r} - (\mathbf{r}_i(t + t') - \mathbf{r}_j(t'))) dt'. \quad (5)$$

Similarly, inserting eq. 5 into eq. 1, we find:

$$F(\mathbf{Q}, t) = \sum_i^N \sum_j^N b_i b_j \int \exp(i\mathbf{Q} \cdot (\mathbf{r}_i(t + t') - \mathbf{r}_j(t'))) dt'. \quad (6)$$

Next, we can rewrite $\exp(i\mathbf{Q} \cdot \mathbf{r}(t))$ as

$$\exp(i\mathbf{Q} \cdot \mathbf{r}(t)) = \int \exp(i\mathbf{Q} \cdot \mathbf{r}(\tau)) \delta(\tau - t) d\tau. \quad (7)$$

Combining equations 6 and 7 with eq. 1, we can do all the integrals over exponentials:

$$S(\mathbf{Q}, \omega) = \sum_i^N \sum_j^N b_i b_j \int \int \exp(i(\mathbf{Q} \cdot \mathbf{r}_i(\tau) - \omega\tau)) \exp(-i(\mathbf{Q} \cdot \mathbf{r}_j(\tau') - \omega\tau')) d\tau d\tau'. \quad (8)$$

Finally, with $\tau \equiv t$, we can rewrite this as

$$S(\mathbf{Q}, \omega) = \left| \sum_i^N b_i \int \exp(i(\mathbf{Q} \cdot \mathbf{r}_i(t) - \frac{E}{\hbar}t)) dt \right|^2. \quad (9)$$

Equation 9 can be evaluated from molecular dynamics trajectories, $\mathbf{r}_i(t)$. An expression similar to eq. 8 has been used in the past [8, 9].

If the experiment uses X-rays instead of neutrons, we need to replace the scattering lengths b_i in eq. 9 by the atomic form factors $f_i(Q)$. The form factors can be approximated by a sum of Gaussians:

$$f_i(Q) = \sum_j^4 p_{i,j} \exp\left(-q_{i,j} \left(\frac{Q}{4\pi}\right)^2\right) + s_i. \quad (10)$$

The parameters $p_{i,j}$, $q_{i,j}$, and s_i for X-rays and the scattering lengths b_i for neutrons are tabulated and can be looked up [10, 11]. The index i runs over all atoms in the simulation cell and $f_i(Q)$ is different for different atoms. Q is the (magnitude of-) momentum transferred from the incident (mono-chromatic) beam into the sample.

An expression similar to eq. 9 has been used with MD to study silicon nano-wires and nano-membranes in the past [8, 9]. However, the expressions in these references are

not “squared” as they should be: for the scattering cross section (which is proportional to $S(\mathbf{Q}, \omega)$) to have to right dimensions, it must be proportional to b^2 . Their expression is not (this is probably just a typo). Moreover, their expressions are only valid for homogenous crystals with one atom type in the simulation (implicitly using units where $b_i \equiv b \equiv 1$).

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