Nuclear kinetic energies from final-state effects in the harmonic limit

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Abstract. This work shows a simple, yet quite powerful, data pre-treatment protocol for mass-resolved neutron spectroscopy, aimed at a better estimation of the main quantum observable linked to a nuclear-momentum distribution, its second moment. From a methodological point of view, the immediate benefit of having such a protocol is twofold. Firstly, a good estimate of a second moment of a nuclear-momentum distribution, and hence nuclear kinetic energy, provided as input for subsequent data fitting, accelerates the convergence of a data fit and minimises the likelihood of it being stuck in a non-physical solution. Secondly, it provides a simple screening tool in the search for quantum systems exhibiting statistically significant departures for a classical behaviour of equipartition of kinetic energy at any given temperature. This second benefit renders the presented protocol an important data screening tool in the search of materials exhibiting exotic properties, possibly attributed to nuclear quantum effects.

1. Introduction

Neutron Compton scattering (NCS), owing to its unique capability to measure nuclear momentum distributions (NMDs) in a mass-resolved manner, has been a method of choice in many material science studies aiming at characterising functional properties related to nuclear quantum effects (NQEs)\cite{1, 2, 3}.

The first step on this journey is a robust prediction of the second moment of NMDs, as well as the related values of nuclear mean kinetic energies. These important nuclear quantum observables have been historically linked to nuclear zero-point energy \cite{3}, which influences many material properties, starting from thermodynamical potentials \cite{4}, through phase boundaries and activation energies for kinetic rate constants and diffusion \cite{5}, and all the way to isotope fractionation ratios and pH values, to be mentioned but a few \cite{6}.

More recently, a few other ‘nuclear quantum yardsticks’ have been developed to characterise the degree in which a given material under investigation is affected by NQEs\cite{1, 2}. The first of them is the ‘nuclear quantum temperature’ which, unlike its thermodynamic counterpart, is a mass-specific property reflecting how the amount of kinetic energy of a given nucleus present in a condensed matter system translates into an equivalent amount of temperature\cite{1, 2}. Recently,
another parameter characterising 'nuclear quantumness' of a system has been proposed, a quantum-energy excess \((\text{QE})\), defined as the ratio of the nuclear kinetic energy measured in an NCS experiment to a classical prediction based on energy equipartition theorem \([7]\). The way the QE is defined is reminiscent of a description provided by Ceriotti when describing the degree in which NQEs play a role in the description of nuclear dynamics of hydrogen and oxygen in liquid ice and water \([8,6]\). To this end, a very striking observation is that even at 750 K atoms in water are far from classical behaviour. Oxygen atoms have kinetic energies 10% higher and hydrogen atoms have nearly double the kinetic energy compared to the classical prediction, giving at this temperature a mean kinetic energy per atom of 97 meV \([8]\). Moreover, even heavier atoms exhibit a considerable amount of QE. In the solid caesium hydrogen sulfide it was found that only the heavier caesium atoms reach the classical limit at room temperature. Contrary to naive expectation, sulfur exhibited a more pronounced quantum character relative to classical predictions than the lighter oxygen atom, which was interpreted as an NQE arising from the tighter binding environment of this species \([7]\).

The examples of nuclear quantum observables and their links to important material properties, mentioned above, constitute a motivation for a robust NCS data pre-treatment protocol aiming at constraining the fitting of the second moments of NMDs to regions in parameter space lying much closer to physically meaningful solutions. Historically, the first attempt with respect to direct kinetic energy extraction from NMDs was made by Senesi \([9]\) by directly, i.e., without resorting to nonlinear fitting of the scattering spectra, employing the sum rules associated with the scattering functions.

The work presented in this contribution represents an extension of this line of NCS work in two important aspects. Firstly, it is a further contribution to the development of the robust and efficient methodology of the extraction of nuclear kinetic energy from experimental NCS data. Secondly, it extends the methodology towards the fitting-free estimation of nuclear kinetic energies in systems with complicated stoichiometry yielding NCS spectra with partially overlapping peaks. The overarching motivation of the presented work is to provide a simple screening tool in the search for quantum systems exhibiting statistically significant departures from a classical behaviour of equipartition of kinetic energy. Such a screening protocol is a much needed tool for system-tailored \textit{ab initio} modelling based on the degree in which NQEs manifest themselves in the NCS data.

This work is organised in the following manner. First, the Sec. 2 describes the basic theoretical assumptions and approximations outlining the concept of the nuclear momentum distribution and its mathematical connection to the expression describing the overall shape of the signal recorded in the time-of-flight (TOF) domain in the neutron Compton scattering technique. Specifically, the Subsecs. 2.1 and 2.2 describe, respectively, how these systematic departures from the basic approximation can be taken into account in a perturbative manner and how they can be employed to infer the information about the widths of the momentum distributions from the peak positions of a TOF spectrum under an assumption of harmonic lattice vibrations.

2. Methodology

2.1. Nuclear momentum distributions from neutron Compton scattering

Detailed accounts of the NCS method, in terms of both its instrumental and mathematical foundations, can be found elsewhere \([1,3,2]\). In this contribution, we will thus concentrate only on the main physical assumptions and mathematical approximations underlying the way NMDs are obtained in NCS, with special emphasis on the description of departures from them, termed as Final-State Effects (FSEs).

In what follows, throughout the rest of the text, we will use terms nuclear momentum distribution and longitudinal momentum distribution interchangeably. Moreover, in what follows the term 'NMD peak position for a given nucleus' will be defined as the position of the NMD
maximum. Mathematically, this means that the NMD peak position is defined for a smooth peak shape as the locus of the place at which the first derivative of the curve describing the peak, calculated with respect to the domain in which the peak is plotted, vanishes. In experimental practice, however, NMD peak positions are rather determined by employing a peak-maximum search algorithm.

We start our description with a brief account of the Impulse Approximation (IA). In an nutshell, the IA is a way of mathematically describing a relatively simple physical reality of the kinematics of collisions of very fast (epithermal) neutron projectiles with the target being the sample placed in a neutron beam, such as the one available at the VESUVIO spectrometer at the ISIS Pulsed Neutron and Muon Source in the United Kingdom [10, 11]. In such fast collision regime, the energy \( E \) and momentum \( q \), transferred from the impinging neutrons to the sample in the scattering process, are sufficiently high (in the range 1–100 eV and 30–200 Å\(^{-1}\), respectively) that the kinematic description boils down essentially to binary collisions between neutrons and individual nuclei present in the sample under investigation. Moreover, such binary collision is, within the IA, governed by energy and momentum conservation [1, 3, 2]. It is this description which underlies the very unique feature of the NCS as a spectroscopic method, that is, its intrinsic mass-selectivity.

Mathematically, the IA is set out using the following chain of approximations. First, the dynamic structure factor \( S(q, E) \), for a given atom of mass \( M \), is reduced to a single peak centered at the recoil energy \( E_r = \hbar^2 q^2 / 2M \) with \( \hbar = 2.0446 \text{ (meV amu)}^{1/2} \AA \) [12, 13, 14, 15, 16, 17, 18, 3]. This first approximation paves the way to the West scaling property of NCS. Namely, a dynamic structure factor, \( S(q, E) \), of a sample consisting of \( N \) different atomic species with different nuclear masses \( M_N \), can be decomposed into \( N \) individual peaks in the domain of the longitudinal-momentum space \( J(y) \) of the respective masses, \( S(q, E) = \sum_{M} (M / \hbar^2 q^2) J_M(y_M) \).

In this decomposition, \( y_M \) is the initial radial momentum \( p \) of the nucleus with mass \( M \) projected onto the scattering vector \( q \), \( J_M(y_M) \) is the so called NCS profile [13, 12] and formally corresponds to the NMD of the target nucleus along \( y_M \).

In this work, motivated by the fact that, in the bulk of present-day NCS work, NQE\(^s\) are simulated using the approximation of harmonically bound isotropic systems [1, 2], we will consider only spherically averaged three-dimensional longitudinal NMDs. In this case, \( J_{IA}(y) \) for a given mass \( M \) in the IA limit depends only on the magnitude of \( y \) but not on \( q \). Moreover, as we want to find a robust way to approximate the second moment of an NMD by obtaining its standard deviation (STD) value, denoted by \( \sigma \). In doing so, we will concentrate on the leading, purely Gaussian term only:

\[
J_{IA}(y) = \frac{1}{\sigma \sqrt{2\pi}} \exp \left( -\frac{y^2}{2\sigma^2} \right),
\]

where \( \sigma \), with the present choice of units, is expressed in Å\(^{-1}\). For finite values of \( q \), corrections to the IA are known as FSE\(^s\) [18, 3]. To account for FSE\(^s\), the method of Sears [12] is routinely incorporated into standard NCS data treatments [18] by expressing the measured NCS profile \( J(y) \) as a series of the form

\[
J(y) = J_{IA}(y) + J_{FSE}(y) = J_{IA}(y) - \frac{M \langle \nabla^2 V \rangle}{36 \hbar^2 q^2} \frac{d^3}{dy^3} J_{IA}(y) + ...
\]

where \( \langle \nabla^2 V \rangle \) is the mean value of the Laplacian of the potential energy of the nucleus expressed in meV Å\(^{-2}\) (cf. Refs. [18, 19]). Importantly, an explicit connection between the magnitude of FSE\(^s\) \( k \) and \( \sigma \) can be established as \( k = \sqrt{2\sigma} / 12 \) [20, 21, 22] with the FSE term, given by the Eq. 2, expressed using the third order Hermite polynomial, \( H_3 \left( \frac{y}{\sigma \sqrt{2}} \right) \). This results with an
expression:

$$J(y) = \frac{1}{\sigma \sqrt{2\pi}} \exp \left( -\frac{y^2}{2\sigma^2} \right) \left[ 1 - \sigma \frac{\sqrt{2}}{12q} H_3 \left( \frac{y}{\sigma \sqrt{2}} \right) \right].$$  \hspace{1cm} (3)

The longitudinal momentum distribution of a given nucleus, $J(y)$, is not directly accessible. Most generally, the starting point for the analysis is the expression describing the count rate, $C_\theta(t)$, of a neutron detector for a scattering angle $\theta$ in the time-of-flight, $t$, that takes explicitly into account the resolution of the instrument. This resolution in most generally incorporated into the expression for $C_\theta(t)$ in the form of multiple integrals, performed independently for each value of the TOF, $t$, over the distributions of geometrical and energy analyser parameters of the spectrometer [23]. In practice, however, a sufficiently good degree of reproduction of experimental spectra is usually achieved by incorporating the instrument resolution in form of sum of convolutions of longitudinal momentum distributions, $J_M(y_M)$, with their respective mass-dependent resolution functions, $R_M(y_M)$, referred to as the Convolution Approximation (CA) [3, 2, 24]:

$$C_\theta(t) = A' \left[ \frac{E_0 I(E_0)}{q} \right] \sum_M I_M M J_M(t) \otimes R_M[y_M(t)]$$  \hspace{1cm} (4)

Equation 4 conveys two important messages about the way in which the information about the NMD is hidden in an NCS experimental spectrum. Both of them are responsible for the difficulties which NCS data treatment faces when trying to predict basic NMD properties, especially at the stage of pre-fitting the initial raw data. The first realisation is that two pre-factors need to be applied to NMD for mass $M$, $J_M(y_M(t))$ given by Eq. (3), to convert it from the domain of the longitudinal momentum $y_M$ into the $t$ domain: (i) $A'$ is a mass-independent experimental constant, and (ii) the mass-independent factor $[E_0 I(E_0)/q]_t$, that depends on the incident neutron spectrum, $I[E_0(t)]$, the initial neutron energy, $E_0(t)$, and the momentum transfer $q(t)$, all explicit functions of $t$. Moreover and most importantly in the context of a robust NMD shape-prediction protocol, the second important feature of the count rate in the time-of-flight domain is that it contains a mass-dependent resolution function which can also be expressed in the domain of the longitudinal momentum, $R_M[y_M(t)]$. In general, this resolution function will smear out the features of the respective NMD profiles associated with the same masses and contribute to decreasing the mass-resolution of the technique by increasing the peak overlap in the spectrum. The resolution function of the instrument is also the reason why one resorts to fitting the time-of-flight spectra using the CA and the models such as the ones described by Eqs. (3) and (4).

The initial stage of NCS data fitting has been described in detail elsewhere [2, 3]. Thus, here only a few aspects of this procedure, relevant for the work presented, will be mentioned. The NCS data pre-treatment relies crucially on the fact that integrated peak intensities, denoted in Eq. 4 as $I_M$, are proportional to the scattering densities $I_M = A N_M 4\pi b^2_M$ where $4\pi b^2_M$ are the total (bound) neutron-scattering cross sections for masses $M$. [25, 18]. First, raw TOF data are usually fitted sequentially, detector by detector, using Eq. (4) in order to obtain the initial values of the fitting coefficients, $I_M$ and $\sigma_M$. Then, the obtained values of $I_M$ and $\sigma_M$ are used as input parameters to calculate the sample-dependent forward scattering corrections: (i) multiple scattering (MS) from the sample and container, and (ii) gamma background (GB) due to cross-talk between signals created at the forward detectors by primary and secondary gold foils. It is at these two first steps of data pre-treatment were the initial good assessment of the values of $\sigma_M$ is crucial. Resorting to fitting the count rates using Eq. 4 will naturally introduce correlations between $I_M$ and $\sigma_M$ as fitting parameters. These correlations will propagate through the whole data pre-fitting process and introduce systematic uncertainties in the shapes of the final NMD curves fitted to isolated recoil peaks after the whole series of correction have been applied to data.
It is thus crucial to develop a robust protocol to predict initial values of $I_M$ and $\sigma_M$, possibly in a way that does not involve non-linear fitting algorithms. The method to derive $I_M$ and $\sigma_M$ directly employing the sum rules formulated for $J_M(y_M)$, historically the first and important step in this direction [9], performs robustly in case of non-overlapping peaks in a spectrum described using Eq. (4). In this work, we pave the way to a protocol that can be applied even in the case of partially overlapping peaks, and based on the fact that the information about $\sigma_M$ is encoded in the magnitudes of the FSEs, as can be seen in Eq. (3). We describe the protocol and its mathematical foundations in the next subsection.

2.2. Nuclear kinetic energies from the positions of the maxima of NMDs in the presence of FSEs

The first important question related to the reconstruction of the NMD properties from experimental NCS data is whether the NMD shape is preserved by the convolution with the experimental resolution function. Mathematically, this question belongs to the group of problems tackled by the so-called ‘scale-space methods’ in image processing [26]. Specifically, the chief question to this end has been whether the number and the structure of local minima and maxima of a curve is altered by the convolution process. Using scale-space terminology, the resolution function $R_M[y_M(t)]$ in the convolution product, $J_M[y_M(t)] \otimes R_M[y_M(t)]$, is a convolution kernel termed as a ‘mollifier’. A perfect, i.e., shape-preserving mollifier can be axiomatically derived by requesting a series of properties to be satisfied. Scale-space axioms led Iijima [27] to derive a Gaussian kernel by requiring linearity, translation invariance, scale invariance, semi-group property, and preservation of positivity. Additionally, the scale-space evolution should not create new level curves when increasing the scale parameter $s$ characterising the mollifier, i.e., $R_M = R_M[y_M(t), s]$. If this is satisfied, iso-intensity linking through the scales is possible and a structure at a coarse scale can (in principle) be traced back to the original image. Koenderink [28] showed that a Gaussian mollifier with standard deviation $\sqrt{s}$ will obey this axiom of ‘non-creation of local extrema’, i.e., no additional extrema will be created in the convolved image as the width $\sqrt{s}$ of the Gaussian mollifier increases [29].

Moreover, a question arises whether convolution preserves the unimodality of a function. In general, unimodality means there is only a single highest value of a given function, i.e., if $a$ is a mode for $f$ then $f(x) < f(a)$ for all $x$. Ibragimov [30] showed that if one of the two functions is logarithmic concave (the logarithm of the function is itself a concave function) their convolution is unimodal. Furthermore, if both are logarithmic concave, so is their convolution [31]. To this end, the Gaussian mollifier plays a central role in image processing and physics as it can be shown to preserve unimodality also [30, 31, 29]. For this reason, in what follows the NCS resolution function will be approximated as a Gaussian, despite the fact that, when expressed in the longitudinal momentum space, $R_M[y_M(t), s]$ exhibits a line shape that can be best approximated by a Voigt profile [18, 10, 32]. There is a multitude of reasons for adopting this approximation. Firstly, both in the case of a Gaussian and Voigt profile, the resolution function is symmetric and centred at the zero value of the longitudinal momentum distribution of a given mass, $M$, $y_M(t) = 0$. In consequence, the locus of the maximum of the recoil peak $J_M[y_M(t)]$ will not be altered by switching between both profiles describing the shape of $R_M[y_M(t)]$. However, the mathematical expression defining this locus will be much simplified when using a Gaussian from of $R_M[y_M(t)]$. Secondly, both Gaussian and Voigt profiles are shape-preserving mollifiers. Both are logarithmic-concave functions and, as such, both preserve the structure of maxima and minima of functions they are convolved with. This ensures that, using both Gaussian and Voigt profiles to describe the resolution function, ensures that no additional minima or maxima of $J_M[y_M(t)]$ are created in the process of the convolution. Finally, it is also worth noting that the so-called double difference technique of NCS data acquisition [33, 34, 35, 36, 37] suppresses the Lorentzian wings of $R_M[y_M(t)]$ to such an extent that it can be described as nearly a
Moreover, the use of uranium, instead of gold foils, as the final energy analyser on VESUVIO leads to $R_M[y_M(t)]$ best described as a purely Gaussian function [18, 10, 32]. Thus, VESUVIO as an instrument, in the limiting case of vanishing Lorentzian part of the final energy resolution function, becomes and example of a perfect Gaussian blurring device from the point of view of image and pattern recognition theory. In passing, it is also worth noting that the 'non-creation of local extrema' axiom, fulfilled by the VESUVIO resolution function, has got one more very important consequence for the analysis of NMDs in systems exhibiting nuclear quantum tunnelling. Namely as noted by Car [38], in such case a theoretical model describing an NMD of a tunnelling nucleus would exhibit nodes. In an NCS experiment a log-convex VESUVIO resolution function would then preserve the nodes of the measured NCS spectrum.

Encouraged by these important results, we can proceed to the description of the protocol to estimate $\sigma_M$ values, and hence the values of nuclear kinetic energy, from the positions of the maxima of the measured longitudinal momentum distributions in the presence of FSEs. In what follows, we will describe two limiting cases: (i) one of an instrument described by a purely Gaussian resolution function, and (ii) a perfect-resolution instrument. In both cases, the starting point is the Gaussian longitudinal momentum distribution for a given nucleus with mass $M$, with FSEs in the harmonic limit, $J_M(y_M)$ described by Eq.( 3). Let us start with the most general case of non-vanishing width, $s$ of the instrument resolution function $R_M(y_M)$ and write its convolution with the $J_M(y_M)$ explicitly:

$$J_M(y_M) \otimes R_M(y_M) = \int_{-\infty}^{\infty} \exp \left( -\frac{(y-u)^2}{2s^2} \right) \left( 1 - \sqrt{2} \sigma \exp \left( -\frac{u^2}{2s^2} \right) \right) \frac{\exp \left( -\frac{u^2}{2s^2} \right)}{\sqrt{2\pi s^2}} du. \quad (5)$$

Differentiating Eq.( 5) with respect to the variable $y$, performing the integral analytically, and equating the resultant expression to zero yields the condition:

$$-\frac{\sqrt{2}}{6} e^{\frac{-q^2}{2(s^2+\sigma^2)^{3/2}}} P(\sigma, s, y, q) = 0 \quad (6)$$

where

$$P(\sigma, s, y, q) = \sigma^4 \left( y^2 - \sigma^2 - s^2 \right)^2 + 2 \left( \sigma^2 + s^2 \right)^2 + 3qy \left( \sigma^2 + s^2 \right)^3 \quad (7)$$

Solving the Eq.( 6) amounts to solving the polynomial equation given by Eq.( 7), that is a multiply nested radical equation. Algebraically, the equation has got four solutions. However, the only physically meaningful solution, $y_{max}(\sigma, s, q)$, has the following form:

$$y_{max}(\sigma, s, q) = -\sigma_{tot} \frac{Q(\sigma, s, q) - \sqrt{24\sigma^2 - Q^2(\sigma, s, q) + \frac{12\sqrt{2}q^3}{\sigma(\sigma, s, q)}}}{2\sqrt{2}\sigma} \quad (8)$$

where $\sigma_{tot}^2 = \sigma^2 + s^2$, and

$$Q(\sigma, s, q) = \sqrt{\frac{8\sigma^3\Sigma^{1/3} + 16\Sigma^{2/3} + (2\Sigma)^{2/3}}{\sigma\Sigma^{1/3}}}, \quad \Sigma(\sigma, s, q) = \sigma \left( 9q^2\sigma_0^6 + \sqrt{R(\sigma, s, q) + 32\sigma^8} \right), \quad (9, 10)$$

and

$$R(\sigma, s, q) = 81q^4\sigma_0^{12} + 576q^2\sigma_0^6\sigma^8 - 1024\sigma^16. \quad (11)$$
In addition to the exact analytic solution provided by Eq. 8, one can obtain an approximate solution by expressing the polynomial in the form

\[
y_{\text{max}} = -\frac{\sigma^4}{3q\sigma_{\text{tot}}^2} \left[ (y_{\text{max}}^2 - \sigma_{\text{tot}}^2)^2 + 2\sigma_{\text{tot}}^4 \right] = F(y_{\text{max}})
\]

Furthermore, we can notice that, based on the fact that an FSE correction only slightly shifts the position that the maximum of an NMD would have otherwise had in the IA limit, \( y_{\text{max}} = 0 \), leads to the condition \( y_{\text{max}}^2 \ll \sigma_{\text{tot}}^2 \). One can therefore obtain an approximate solution to be refined through an iterating process. In particular, one has

\[
y_{\text{max}}^{(0)} = -\frac{\sigma^4}{q\sigma_{\text{tot}}^2} \simeq \frac{\sigma^2}{q},
\]

where the last term on the right-hand side is expressed in the limit \( s \to 0 \). By inserting this result in the right-hand side of equation 12, one can define a recurrence relation

\[
y_{\text{max}}^{(n)} = F\left(y_{\text{max}}^{(n-1)}\right)
\]

It is worth noting that the solution of Eq.(8) does not explicitly depend on the recoiling nuclear mass \( M \) although the nuclear mass dependence is implicitly included in the definition of the West scaling variable \( y \). Naturally, the solution can always be plotted in region of \( q \) and \( \sigma \) relevant for a given nuclear mass under investigation. In case of protons, this region is defined by \( q \) stretching from \( q \approx 25 \, \text{Å}^{-1} \) to \( q \approx 125 \, \text{Å}^{-1} \) and \( \sigma \) in the region of \( \sigma \approx 4 \, \text{Å}^{-1} \) to \( \sigma \approx 6 \, \text{Å}^{-1} \). It is this region, for which the solution given by the Eq.(8) in the limit of vanishing \( s \to 0 \) is plotted in Figures 1 and 2. For lighter masses, e.g. proton, deuteron, or lithium, the NCS scattering is by no means elastic [3, 2] and the position of the maximum starts depending non-linearly on the STD, especially for small values of the STD, i.e. for protons (see Fig. 2, bottom).

The next question that arises in the NCS experimental practice is how the position of the maximum of the experimentally observed NMD depends on the width of the resolution function, \( s \). First thing to note to this end is that the width of the VESUVIO resolution function, \( R(y_M) \), when expressed in the longitudinal momentum space of a given nucleus, is proven to vary as a function of the scattering angle, and thus the magnitude of the momentum transfer [18, 10, 32]. This variation is more pronounced for the case of the proton resolution function, where the component responsible for the variation is the angular resolution, whereas in case of heavier masses the dominating contribution, the energy resolution function, is shown to vary relatively less as a function of the momentum transfer [18, 10, 32]. The plot of the position of the maximum of the experimentally observed longitudinal momentum distribution as a function of the width of the resolution function in the longitudinal momentum space is shown in Figure 3. The plot has been generated using Eq.(8) for the value of the width of the proton longitudinal momentum distribution fixed at, \( \sigma = 4.5 \, \text{Å}^{-1} \), a value typical for many condensed matter systems containing protons [2, 3]. Moreover, for the sake of the discussion, the plot is shown for a wide range of the values of the widths of the resolution function. However, a typical value of the width of the instrument resolution function, \( s \), expressed in the proton longitudinal momentum space, is \( s = 1.7 \, \text{Å}^{-1} \).

It can be seen that VESUVIO, due to kinematic constraints imposed on the instrument in order to be able to operate within the IA, presents a lucky case as far as the method described here is concerned. Namely, the main values of the resolution functions of the proton, deuteron and lithium are all located in the high \( q \), low \( s \) region, whereas the the resolution functions of the heavyweight nuclei have their main values located in the low \( q \), high \( s \) region [18, 10, 32].
Figure 1. Positions of the maximum of a Gaussian NMD with FSEs calculated within harmonic limit, given by Eq. (8), for the case of perfect instrument resolution $s \rightarrow 0$. See text for details.

In both those cases, the position of the maximum of the longitudinal momentum distribution practically does not depend on $q$ and $s$, i.e., the method proves to be robust. It is also worth mentioning that this lack of sensitivity to the $q$ and $s$ values is observed (plots not shown here) in the entire region of the STDs of NMD of relevance, i.e., $\sigma = 4.5 - 30 \text{ Å}^{-1}$ [18, 10, 32].

2.3. Experimental Results

All NCS measurements were performed on the VESUVIO spectrometer at the ISIS Pulsed Neutron and Muon Source, United Kingdom [10, 11, 32]. The experimental protocol and NCS data reduction and treatment have been described in great detail elsewhere in the literature [10, 11, 32, 3, 2]. As the method described here differs to some extent from the normally applied NCS data analysis, in what follows we will only concentrate and emphasise those data treatment aspects that are crucial for the understanding of the method.

The starting point for the analysis are raw NCS data obtained in the time-of-flight ($t$) domain and described by the count rate, $C_\theta(t)$, of a neutron detector for a scattering angle $\theta$ [3, 2], given by Eq. 4 with the NMD for mass $M$, $J_M(y_M(t))$, is given, in the IA limit with harmonic FSEs, by the Eq. (5).

The method, for a given nucleus with the mass $M$, can be summarised in the following steps:

- raw TOF data, recorded by a given detector (placed at a given scattering angle $\theta$), are transformed into the longitudinal momentum domain $y_M$;
- a peak search algorithm, implemented in the MantidPlot software [39], is performed in the $y_M$ domain, capitalising on the fact that the expected peak position, to within the algorithm search radius, is expected around $y_M \sim 0$;
- a value of the momentum transfer magnitude $q = q_{max}$ is found numerically for a given value $y_M = y_{max}$, corresponding to the peak centre found by the algorithm in the previous step;
- both values, $[q_{max}, y_{max}]$, are recorded and the procedure is repeated for the next detector;
Figure 2. (a) Curves representing the loci of the maxima of the longitudinal momentum distributions, $J(y)$, calculated using Eq. (8), assuming a perfect instrument resolution function with the vanishing width, $s \to 0$. The loci are calculated as functions of the momentum transfer magnitudes at peak maxima, $q$, calculated keeping the values of the standard deviations of the Gaussian momentum distributions, $\sigma$, constant (see figure legend for the values of $\sigma$). The values of $\sigma$, $q$, and the loci of the maxima of the longitudinal momentum distributions are all expressed in the units of Å$^{-1}$.

(b) Curves representing the loci of the maxima of the longitudinal momentum distributions, $J(y)$, calculated using Eq. (8), assuming a perfect instrument resolution function with the vanishing width, $s \to 0$. The loci are calculated as functions of the values of the standard deviations of the Gaussian momentum distributions, $\sigma$, calculated keeping the values of the momentum transfer magnitudes at peak maxima, $q$, constant (see figure legend for the values of $q$). The values of $\sigma$, $q$, and the loci of the maxima of the longitudinal momentum distributions are all expressed in the units of Å$^{-1}$. See text for details.
Figure 3. Positions of the maximum of Gaussian NMD with FSEs calculated within harmonic limit as a function of the instrument resolution width $s$, expressed in the longitudinal momentum space. The plot has been generated using Eq. (8) with $\sigma = 4.5 \, \text{Å}^{-1}$, a value typical for proton, for which a typical value of the resolution function width $s$ is $1.7 \, \text{Å}^{-1}$ [3, 2]. See text for details.

- the peak maximum loci are fitted with the function given by Eq. (8). In fitting, the parameter, $s_M$, is fixed at the average of all detectors value of $s_M$. Two parameters are free in fitting. The first one is the width of the nuclear momentum distribution, $\sigma$. The second one is, $y_0$, accounting for a small albeit systematic shift of the recoil peak positions due to slightly imperfect instrument calibration. A similar parameter is routinely used in fitting NMDs in NCS [3, 2].

In what follows, two different grouping protocols are described: (i) a sequential, detector-by-detector procedure with no detector grouping; and (ii) a procedure whereby signals are first grouped according to detector bank grouping [10, 11, 32], i.e., in groups of 8 detectors for forward scattering, and 6 detectors for backscattering data. All data analysis steps described here have been performed within the MantidPlot software [39, 40, 41, 42].

3. Results and Discussion
The proposed method has been tested on raw proton NCS data from a recent VESUVIO experiment on solid formic acid (FA) at a temperature of 240 K [22]. As a preliminary step of the analysis, the basic assumption of the proposed method were checked. The result of this preliminary assessment are plotted in Figure 4. The figure shows the result of the sequential, applied detector-by-detector, application of the procedure. No detector grouping of the recorded spectra was performed. The only intervention was that a group of few forward scattering detectors, with low counting statistics was excluded from analysis by masking them in MantidPlot data analysis procedure. This preliminary analysis shows that: (i) the positions of the proton recoil peak maxima do vary significantly with the magnitude of the momentum transfer, $q$ from the neutrons, different from detector to detector (Figure 4, top); (ii) the width of the instrument resolution function exhibits very small variations with the detector number and the assumption of using its averaged over all set of detectors value is certainly justified.
Figure 4. Kinematic range relevant to the NCS experiment on protons in solid formic acid at 240 K [22]. Top: the experimental longitudinal momentum distribution profile, \( J(y_H) \) plotted as a function of the momentum transfer magnitude, \( q \) for forward scattering Vesuvio detectors. Middle: the proton resolution function, \( R(y_H) \) plotted as a function of the proton longitudinal momentum, \( y_H \). Bottom: \( J(y_H) \) plotted as a function of \( y_H \) for forward scattering Vesuvio detectors. Black streaks with no scattering intensity in the top and bottom figure panels correspond to masked detectors. See text for details.

(Figure 4, middle); and (iii) the positions of the proton recoil peak maxima, when plotted in the proton longitudinal momentum domain, do exhibit small albeit pronounced variation with the detector number and thus with the value of the momentum transfer, \( q \) (Figure 4, bottom).

It can be clearly seen in Figure 4 that whereas the position of the maximum of proton NMD in FA proves to depend very sensitively on the magnitude of the momentum transfer \( q \) (top panel), the dependence is much less pronounced on the longitudinal momentum variable \( y_H \) (bottom panel). Moreover, as shown in the inset in the middle panel of Figure 4, a Gaussian fit to the averaged over the whole set of forward scattering detectors instrument resolution function for the proton is of very good quality, yielding the value of the width of the averaged resolution function, \( s = 4.2 \, \text{Å}^{-1} \).

The result of the fit of the position of the maximum of the proton longitudinal momentum
distribution in FA at 240 K is shown in Figure 5. The STD of the proton NMD, obtained from the fit to the data with the width of the resolution function fixed, $s = 4.2 \text{ Å}^{-1}$, was $\sigma = 4.5 \pm 0.6 \text{ Å}^{-1}$, very well within a single standard deviation value in agreement with the value published for FA at 240K, being $\sigma = 4.4 \pm 0.1 \text{ Å}^{-1}$ [22].

The relatively big scatter of the data, giving the relative standard deviation of 10% of the value of the STD of the proton NMD, is the result of the data grouping policy. Thus, an attempt was made, to re-fit the data by grouping data in groups of 8 detectors, corresponding to the VESUVIO detector bank setup in forward scattering. The result of this procedure is shown in the right panel of Figure 5. A much better fit quality is obtained with the value of $\sigma = 4.5 \pm 0.3 \text{ Å}^{-1}$. Thus, detector grouping improves the fit quality by reducing the error of the STD of the NMD by a factor of two.

4. Summary
On the whole, this work aligns itself closely with the overall direction in the research centered around electron-volt neutron spectroscopy by simultaneously addressing its two mainstream problems. Firstly, it paves the way towards high-throughput NCS data processing by offering a simple yet robust data pre-treatment protocol. Secondly, it provides a solid springboard towards more robust benchmarking of modern ab initio code simulation results for solid state systems and molecules.

To this end, we have presented a robust NCS data pre-fitting protocol that aims at obtaining the good initial guess of the second moments of NMDs for further NCS data processing and modelling. The method can be summarised in two steps. These steps are identical for each nuclear mass for which a recoil peak can be clearly resolved in the NCS spectrum recorded by each detector. Moreover, all the steps can be performed either on the detector-by-detector basis, or alternatively, stepping over a set of grouped detectors (e.g., in groups of corresponding to
In the first step, a peak-finding algorithm is employed to find the positions of recoil peaks. As a result of this step, a set of pairs of values, $q_{\text{max}}, y_{\text{max}}$, is found, corresponding to the values of the recoil peak maxima positions, expressed in the domain of the longitudinal momentum of a chosen nucleus, $y_{\text{max}}$, and the values of the magnitudes of the momentum transfers, $q_{\text{max}}$, from the incident neutrons to the recoiling nucleus that correspond to those recoil peak positions.

Following this, the points on the plot of $q_{\text{max}}$ vs. $y_{\text{max}}$ are fitted with the function given by Eq.(8), keeping the width of the instrument resolution function fixed and introducing two parameters free in fitting. These free parameters are the width of the nuclear momentum distribution, $\sigma$, and, $y_0$, accounting for a small albeit systematic shift of the recoil peak positions due to slightly imperfect instrument calibration.

The procedure does not require any detailed knowledge of the precise shape of the NMDs as it relies on the approximation of a given NMD by a Gaussian term with FSEs calculated in the harmonic limit. The method can be applied for different detector grouping policies, both in forward and backscattering regimes of the VESUVIO spectrometer. The method owes its robustness to the fact that NMD data are sampled at their maxima where the influence of noise, sample-dependent and independent background signals and the overlap with NMDs of other nuclei are minimal.

Promising results, obtained for proton NMDs in solid FA show that, grouping detectors by banks, in order to reduce the data sparsity, yields results that are of overall good quality and well within the values obtained by much more complicated sequential NCS data fitting protocol, with sample-dependent data corrections to account for multiple scattering and neutron gamma background, followed by data grouping in momentum space. However, the proposed method can only serve as a preliminary step in the NCS data reduction scheme. For precision work, aiming at a detailed characterisation of the shapes of NMDs, a fully-fledged data reduction and fitting protocol, including all the above mentioned corrections, cannot be avoided.

The proposed method can be applied in case of extensive parametric NCS measurements, as a diagnostic tool in search of NMD changes induced by phase transitions or other changes in physical sample properties as a function of external stimuli such as temperature, pressure, or pH value of the environment.

On the ab initio materials modelling front, the method proposed and described here can serve as yet another much-desired data screening tool. Namely, the method can capture systematic deviations from the final states effects within the harmonic lattice approximation. To this end, it serves potentially an important role as a filter selecting experimental results potentially requiring time consuming and complicated ab initio modelling beyond the harmonic lattice approximation limit. Conversely, when successful in data pre-fitting, it can contribute to avoiding time consuming modelling approach all together, thus providing a much-sought tool for material modelling community. In doing so, the method contributes further to the optimisation of the synergy between neutron Compton scattering and materials modelling.

Moreover, the proposed method can be also applied as a diagnostic tool in the assessment of the overall quality of the instrument calibration. To this end, any trends that will not be captured by the fitting curve with a single offset parameter may signal that a re-assessment of instrument calibration is needed. For such an assessment, a set of well-known calibration samples can be employed with their second moments of nuclear momentum distributions fixed in fitting during the calibration procedure.

5. Outlook
Estimation of the second moment of NMDs with the sheer knowledge of the recoil positions is potentially a very robust and quick data screening tool for both experimental and ab initio NCS data modelling. To this end, further method improvements are highly desired.
The first obvious step in this direction is the optimisation of detector signal grouping prior to the analysis of the recoil peak positions. To this end, a Bayesian-like approach may additionally be implemented, to optimise the data grouping protocol given a degree of data sparsity, in a mass-resolved manner [43, 44].

Furthermore, additional work is needed to assess the performance of the method for higher masses, both in forward and backscattering. This part of work is also necessary in case of NCS spectra recorded using samples with complicated stoichiometry with NCS spectra consisting of overlapping peaks. In such case, the above mentioned Bayesian approach together with novel peak search algorithms should be tested, preferably within the MantidPlot data simulation and treatment environment.

Further improvement of the precision of the proposed method, both as NMD data pre-fitting and instrument calibration procedure, can be obtained by relaxing the constraint of the constant instrument resolution function. In principle, a two-dimensional data surface-fit can be performed with both, the magnitude of the momentum transfer at peak position and the width of the resolution function calculated individually.

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