What is the structure of liquid Bismuth?

El'ad N Caspi, Yaron Greenberg, Eyal Yahel, Brigitte Beuneu, Guy Makov

1Physics Department, Nuclear Research Centre-Negev, 84190 Beer-Sheva, Israel
2Laboratoire Léon Brillouin (CEA-CNRS), CEA/Saclay – 91191 Gif-sur-Yvette
cedex, France, EU
3Materials Engineering Department, Ben-Gurion University of the Negev, 84105
Beer-Sheva, Israel
caspie@nrcn.org.il

Abstract. The structure of liquid Bismuth is probably the best-studied among elemental liquid
metals because of a combination of the interesting physical properties of Bismuth and its
excellent neutron scattering properties. Over the last six decades there have been more than 10
independent studies of the structure of liquid Bi, near the melting temperature. This remarkable
number of measurements provides an opportunity to compare these results and to analyze the
different sources of error contributing to the calculated pair distribution function. In the present
contribution we analyze possible sources of error by varying the analysis procedure for a given
measurement. By repeating a previous measurement in a new experimental configuration we
demonstrate that an invariant (i.e. up to an absolute error) structure factor can be obtained.
Transforming the structure factor into the radial distribution introduces new sources of error
which causes the scatter to be greater than that required to resolve issues such as the existence
of liquid-liquid phase transitions in Bi and to obtain correlation between thermo-physical
properties and structure. We consider the contribution of different parameters when
transforming the structure factor to the radial distribution function.

1. Introduction

In the last decade the structure of liquids has received renewed attention in the context of liquid-liquid
phase transitions (LLPT) and anomalous thermo-physical properties [cf. 1-5]. These phenomena are
probably associated with small changes in the three dimensional liquid structure. The most common
method to describe the structure of the liquid is through the radial distribution function (RDF), which
is a limited one dimensional representation of the full three dimensional structure. Identification of
small changes in the three-dimensional liquid structure by their effect on the RDF requires its
knowledge to high accuracies.

This challenge is even greater when we consider that the RDF cannot be measured directly in real
space. Instead, diffraction patterns from the liquid are collected and the liquid structure factor is then
obtained by a series of approximations to account for incoherent scattering, multiple scattering,
inelastic scattering (in the case of neutron diffraction), Compton scattering (in the case of X-ray
diffraction), absorption, and scattering by the experimental setup. All these issues have been known
for a long time and a standard set of procedures has been developed to analyze the experimental data
and extract the structure factor. Following the application of these correction procedures, the
accumulating systematic error in the case of neutron scattering from heavy elements is of the order of 4-5% [6-9].

To determine the RDF from the structure factor an additional error is introduced by the use of finite range in the momentum transfer, q, space. This finite cutoff introduces errors into the RDF, most notably short wavelength oscillations, which may be considered as numerical noise. These oscillations may affect the interpretation of the RDF, and in particular prevent identification of small changes therein. Several attempts have been made in the literature to propose procedures which reduce this source of error in the RDF, but it has not been possible to eliminate it [10,11].

Bismuth is an ideal element for neutron scattering measurements due to its high coherent scattering cross-section (9.1477 barns), its negligible incoherent scattering cross-section (0.0084 barns), and a very small absorption cross-section (0.0338 barns at λ=1.8 Å). Adding these unique properties to the bismuth relatively low melting temperature (~550 K) made this element the focus of a relatively large number of neutron scattering studies in its liquid phase [cf. 5,9,12-17]. Moreover, the bismuth’s rather complex pressure-temperature phases diagram both in the liquid, and in the solid states [1] enhances researchers interests in its physical properties in elevated temperature and pressure.

In the present work, we report on two separate studies of the structure of liquid Bi at ambient pressure that we have performed at the 7C2 diffractometer at Saclay, using different experimental setups, separated in time by 5 years, and show that the structure factors obtained agree to better than 1%, thus establishing the consistency of our analysis procedures. Using this structure factor as a reference, we compare a large number of experimental studies of liquid Bi at ambient pressure in order to investigate the experimental scatter in the structure factor and find out its significance. We then explore how the errors in the experimental determination of the structure factor affect the calculated RDF, focusing on two main issues: sensitivity to convergence in the high q range and choice of qmax.

2. Experimental setup

We have measured the structure factor of liquid bismuth near the melting point on two different occasions, separated over 5 years, at the 7C2 diffractometer at Saclay. In both experiments the neutron wavelength was ~0.7 Å, and the detector setup was similar. However, the experimental setup in the vicinity of the sample was significantly different between the two experiments.

In the first experiment, dated to 2006 [5], the sample was placed inside an 8 mm inner-diameter quartz tube, with walls thickness of 1 mm. The sample-holder assembly was placed inside a cylindrical double walled vanadium furnace, the inner diameter of each wall being 30 mm, and 90 mm. The dimensions of the neutron collimator close to the sample (in the upstream direction) were 10 cm × 5 cm × 1.2 cm (L×H×W).

In the second experiment, dated to 2011, the sample was placed inside a 10 mm inner-diameter quartz tube, with walls thickness of 1 mm. The sample-holder assembly was placed inside a cylindrical single walled vanadium furnace, the inner diameter the wall being 30 mm. The dimensions of the neutron collimator close to the sample (in the upstream direction) were 10 cm × 5 cm × 1.6 cm (L×H×W).

It is worth noting that between the years 2006, and 2011 the 7C2 diffractometer and its monochromator were twice removed for maintenance, and then were reassembled and recalibrated.

Even though the above mentioned differences are significant in an experiment aiming at the absolute measurement of the structure factor, the form of the corrections and the analysis procedures applied in both measurements were identical with the exception of the different experimental parameters used. Thus, in both experiments we performed conventional data reductions for background, cell, and furnace contributions, incoherent, multiple, and inelastic scattering [6-8].
3. Results

3.1. Structure factor – S(q)

The validity of the procedure described above can be determined by requiring that different experimental measurements of I(q) produce the same structure factor. This comparison is difficult to achieve, since the corrections to the measured signal applied by different researchers are not identical, nor are the details of the analysis procedures.

In this work, we have the opportunity to compare our two independent measurements separated over 5 years using different setups, on the same instrument. This comparison can be undertaken to a high accuracy, while removing extraneous, non-physical sources of experimental scatter. Before comparing the two measurements we first determine their statistical convergence.

In Figure 1 we present the structure factor as determined in a series of measurements taken over different collection times. We see, trivially, that the experimental signal to noise ratio decreases as the collection time is increased. More significantly, we see that the signal to noise ratio decreases as the transferred momentum, q, increases, reflecting the strong momentum dependence of the atomic scattering function. Specifically, in the high q region the signal has very weak q dependence so we can estimate the signal to noise ratio quantitatively. As an example, the signal in our S(q) data, collected over 6 hours (Figure 1) at q=12.4 Å\(^{-1}\), equals (S(q)-1)≈0.01. The statistical noise in that region can be estimated from the scatter of the data points, and is roughly 0.003 for one standard deviation (σ). As we will see later this high q signal to noise ratio could be used as an indicator for the statistical quality of the measured S(q).

![Figure 1. An example of the statistical convergence of the structure factor, S(q), of liquid bismuth measured on the 7C2 neutron diffractometer at 2006. Results from 1 hour, 2 hours, and 6 hours measurement of data collection of the same experiment are depicted.](image-url)

Having established the statistical convergence, we now proceed to compare the two experimental determinations (from 2006, and 2011) of the liquid bismuth structure factor S(q) presented in Figure 2. We see that the results are in excellent agreement to better than 1% i.e the differences are of the order of the statistical noise. Thus, we have an indication that the structure factor obtained by our data...
analysis procedures in these two different experiments is indeed the physical structure factor. Nevertheless, since the analysis methods were the same in both cases a systematic error due to uncertainties in the overall 7C2 diffractometer setup, the knowledge of the exact dimensions of sample holder, furnace, and sample chamber within the beam path used for the absorption corrections [6], and the approximation made in the inelastic scattering corrections [8], cannot be ruled out.

![Graph showing Bi @553K](image)

**Figure 2.** Comparison of two measurements of liquid bismuth structure factor, S(q), undertaken on the 7C2 neutron diffractometer at Saclay. The ratio of the S(q) signals is presented in the inset and shows that the deviation between the two measurements is typically less than 1%.

Having established that we have an estimate of the true physical structure factor, we compare our results with previous studies over the last 60 years, shown in Figure 3a.

![Graph showing liquid Bi near melting point](image)

**Figure 3.** (a) Representation of different experimental determinations of the structure factor of liquid bismuth near the melting point over the last 60 years. (b) The high q range of the structure factor. The arrow indicates the maximal momentum transfer, q, measured in all but our measurements.
We see that the positions of the maxima and minima are essentially the same over 60 years of measurements, as expected from the relatively exact determination of the momentum transfer in diffraction measurements. In contrast, the amplitude of S(q) varies considerably between the measurements across the years. The magnitude of the variation is approximately 30% in (S(q)-1) even for the first peak in S(q). Moreover, relative scatter between measurements increases with increasing q. Finally, all measurements reduce to noise with the typical q\textsubscript{max} of 10 Å\textsuperscript{-1}, with the exception of our results at 7C2 which extend to approximately 14 Å\textsuperscript{-1} keeping a reasonable signal to noise ratio (see Figure 3b).

3.2. Radial distribution function – G(r)

The RDF, G(r), is the manifestation in direct space of the structure factor and as such is easier to interpret as representing a one dimensional average liquid structure. However, due to the experimental constraints, S(q) can be determined up to a certain q\textsubscript{max} value. This may prompt the question of how to obtain the “best” representation of G(r) from the limited data. A naïve approach might be to use the maximum amount of q range available in the data, and, trivially, to aim for the longest measurement time.

The effect of measurement statistical noise in determining the structure factor on the RDF is negligible as can be seen from Figure 4 where we compare the RDFs obtained from structure factors measured by us with twice and six times the number of neutron counts. A small effect of the increased measurement time is a reduction in the amplitude of the oscillations in G(r), especially pronounced in the shoulder region (4-5Å).

![Figure 4](image_url)

**Figure 4.** Calculation of the RDF, G(r), using 1, 2, and 6 hour S(q) measured in the 2006 neutron diffraction experiment on the 7C2 diffractometer at Saclay.

In Figure 5, we see that increasing the cut-off wavevector, q\textsubscript{max}, used to obtain the RDF, does not lead to a monotonous decrease of the amplitude of the data oscillations. Instead, we find that the oscillations in the RDF associated with the finite q-space measurements may increase with increasing q\textsubscript{max} (Figure 5). We note that the main impact of the oscillations is in the region between the first and second hard sphere peaks in the RDF. This is to be expected as the high q range in the structure factor...
affects mainly the finer details of the liquid structure, such as the existence of shoulder, or hump between the 1st and 2nd hard sphere peaks in G(r) in anomalous liquid metals [5,20].

![Liquid bismuth RDF as determined from the S(q) measured at 2006 on the 7C2 diffractometer at Saclay. Different curves represent different q_{\text{max}} cut-offs in the S(q) data. A positive node is when S(q_{\text{max}})=1, and dS(q)/dq>0 (at q=q_{\text{max}}). A negative mode is when S(q_{\text{max}})=1, and dS(q)/dq<0 (at q=q_{\text{max}}).](image)

**Figure 5.** Liquid bismuth RDF as determined from the S(q) measured at 2006 on the 7C2 diffractometer at Saclay. Different curves represent different q_{\text{max}} cut-offs in the S(q) data. A positive node is when S(q_{\text{max}})=1, and dS(q)/dq>0 (at q=q_{\text{max}}). A negative mode is when S(q_{\text{max}})=1, and dS(q)/dq<0 (at q=q_{\text{max}}).

Further progress may be obtained if we consider the effect on the calculation of G(r) of using different cut-off values [q_{\text{max}} at the S(q) measured data] at selected positions from a positive to negative node in S(q) (cf. Figure 3). We see that choosing the cut-off at a node, i.e. at S(q_{\text{max}})=1, leads to a reduction in the oscillations (Figure 5) with better results at a positive node. However, choosing the cut-off at the highest available positive node in the data requires some caution if the chosen q_{\text{max}} is in the region where the statistical noise is too high. In our case, choosing the cut-off at the positive node q_{\text{max}}=13.8 Å^{-1} (Figure 1) leads to high numerical oscillations (Figure 5).

The sensitivity of G(r) to q_{\text{max}} is examined by considering alternative choices determined by the positive nodes of S(q) (Figure 6). We see that as expected from the analysis above, as q_{\text{max}} is increased the results for G(r) converge and the oscillations are reduced. From these results we see that measurements limited to 10 Å^{-1} still introduce a spurious contribution to the RDF, which is significantly reduced, but not eliminated at 11.8 Å^{-1} (Figure 6).

4. Discussion
We have shown that the structure factor can be determined up to an accuracy determined by the statistical noise and should not be limited by inconsistencies in the data analysis procedures. This does not mean that this is the exact physical structure factor as there can be systematic methodological errors which may only be uncovered by detailed comparison with determinations of the structure factor by other independent means, such as X-ray diffraction. Such a comparison is beyond the scope of the present work.
The RDF is well-known to be sensitive to the S(q) data cut-off limit, i.e. \( q_{\text{max}} \) up to which the S(q) data is chosen for the calculation of G(r). We see that extending the measurement range in q space, even significantly, does not ensure convergence of the RDF. We also note that statistical convergence does not in itself ensures the convergence of the RDF, which is also affected by the choice of \( q_{\text{max}} \).

**Figure 6.** Liquid bismuth RDF as determined from the S(q) measured at 2006 on the 7C2 diffractometer at Saclay. Different curves represent different \( q_{\text{max}} \) cut-offs in the S(q) data. In this case all cut-offs were chosen at a positive node, i.e. \( S(q_{\text{max}}) = 1 \), and \( dS(q)/dq > 0 \) (at \( q = q_{\text{max}} \)).

A more detailed analysis of the choice of \( q_{\text{max}} \) shows that if it is located at a node defined by \( S(q_{\text{max}}) = 1 \), the spurious wavelengths introduced by the Fourier transform are reduced. We start from the well known definition of the exact RDF [cf. 16],

\[
G(r) = 1 + \frac{1}{(2\pi r \rho)} \int_0^\infty dq q S(q) - 1 \sin(qr) \quad (1)
\]

where \( \rho \) is the atomic density. We now define \( G(r,q_{\text{max}}) \), as the experimental RDF obtained from Fourier transforming the measured S(q) data up to \( q_{\text{max}} \). The error in \( G(r,q_{\text{max}}) \), \( \varepsilon \), is defined by \( \varepsilon(r,q_{\text{max}}) = G(r,q_{\text{max}}) - G(r) \), and it is a function describing the oscillations about the exact G(r). These oscillations vary in wavelength and amplitude with \( q_{\text{max}} \). As \( q_{\text{max}} \) is increased the oscillations vary. This variation may be estimated by considering the locations of the extrema of the oscillations obtained from (after leaving out the constants multiplying the integral),

\[
\frac{\partial \varepsilon}{\partial r} = \frac{\partial G(r)}{\partial r} - \frac{\partial G(r,q_{\text{max}})}{\partial r} = \int_{q_{\text{max}}}^\infty dq q S(q) - 1 \frac{qr \cos qr - \sin qr}{(qr)^2} = 0 \quad (2)
\]

to be insensitive to choice of \( q_{\text{max}} \), i.e. requiring that,
\[
\frac{\partial}{\partial q_{\text{max}}} \left( \frac{\partial \epsilon}{\partial r} \right) = 0 = q_{\text{max}}^3 (S(q_{\text{max}}) - 1) q_{\text{max}}^r \cos q_{\text{max}}^r - \sin q_{\text{max}}^r \\
\left( q_{\text{max}}^r \right)^3 
\]

(3)

This requirement is met if we choose \( q_{\text{max}} \) at a node, i.e. at \( S(q_{\text{max}}) = 1 \). If we introduce the further requirement that the magnitude of variations in \( \partial \epsilon / \partial r \) is minimal, i.e.,

\[
\frac{\partial^2}{\partial q_{\text{max}}^2} \left( \frac{\partial \epsilon}{\partial r} \right) = \frac{\partial}{\partial q_{\text{max}}} \left( q_{\text{max}}^3 (S(q_{\text{max}}) - 1) q_{\text{max}}^r \cos q_{\text{max}}^r - \sin q_{\text{max}}^r \right) > 0 
\]

(4)

this condition is met at a node, if \( S'(q_{\text{max}}) > 0 \), i.e. the node is positive. Thus, we come to the conclusion that the optimal choice of \( q_{\text{max}} \) is at the largest value of a positive node of \( S(q) \) at which the signal to noise ratio is acceptable.

This conclusion also suggests a criterion for determining the signal to noise required at the experiment. The noise should be considerably less than the signal \( \text{abs}(S(q)-1) \) determined at the minimum before \( q_{\text{max}} \), e.g., in our case if \( q_{\text{max}} = 11.8 \text{ Å}^{-1} \) then the noise should be considerably less than the signal of ~0.01. Returning to our experimental data as shown in Figure 1 we see that in our 6 hours run the scatter of data points in the vicinity of \( q = 11.8 \text{ Å}^{-1} \pm 0.003 \text{ Å}^{-1} \) for one standard deviation, three times less than the value of the signal.

5. Conclusions
Due to its excellent neutron scattering properties, its rather low melting temperature, and its complex solid and liquid phase diagrams, the structure factor, \( S(q) \), of liquid bismuth was studied extensively by means of neutron scattering over the last 6 decades. No less than 10 different measurements were undertaken at ambient pressure and near the melting point temperature, with additional studies conducted over the years as a function of pressure, temperature, and alloying \cite{18,19}.

Therefore, liquid bismuth presents a good study ground for the re-examination of error propagation and the main uncertainties (statistical, and systematical) in the process of obtaining \( S(q) \), and from it the RDF by neutron scattering. In this context, we focus here on the comparison of the determination of liquid bismuth \( S(q) \) over the years, and on the numerical error propagating into the calculation of the RDF from it.

We suggest the requirements on the accuracy needed in measuring \( S(q) \) for adequate \( G(r) \) calculations: choosing the highest value of “positive-node” \( q_{\text{max}} \) in the \( S(q) \) data, while keeping significant (factor of 3) signal to noise ratio in the dip (peak) just before (after) this \( q_{\text{max}} \) value. Moreover, we demonstrate here how the measurement of \( S(q) \) up to a \( q_{\text{max}} \) value, which is too low, hinders the ability to study the fine details in the calculated RDF, even when the statistics of the measured \( S(q) \) is adequate. We would like to stress, that it is only through careful study of liquid structure factors up to large \( q_{\text{max}} \) that it will be possible to identify the small structural changes occurring in liquids.

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