A Method of Reducing Termination Errors in Radial Distribution Functions

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Abstract

The radial distribution function \( g(r) \) of a liquid can be obtained from an integral transform of its X-ray scattering intensity \( I(\mu) \). Experimentally, \( I(\mu) \) can be measured over only a limited range, leading to termination errors in \( g(r) \). Using the strict positivity of \( g(r) \), an iterative method is proposed to reduce these errors. The negative portions of each successive distorted approximation of \( g(r) \) are replaced by the value zero and this function is used to generate \( I(p) \) in the non-measured range. Computer calculations on a model function yield encouraging results. The method appears to have an advantage over current approaches as it does not require a knowledge of the hard-core diameter of the atoms. It is also expected to work in the case of molecular liquids where there are some difficulties in applying the current methods.

1. Introduction

The structure of a liquid or an amorphous solid† can be described in terms of the radial distribution function \( g(r) \), which is proportional to the probability of finding an atom per unit volume at a distance \( r \) from another given atom, the proportionality being fixed so that the function has the value of unity at large values of \( r \). The radial distribution function of a liquid can be obtained from an X-ray scattering experiment through the transformation (see e.g. James, 1948)

\[
4\pi\rho_0[g(r) - 1] = \int_0^\infty \mu(\mu) \sin \mu r \, d\mu ,
\]

where \( \rho_0 \) is the atomic density of the liquid and \( \mu \) is related to the scattering angle \( 2\theta \) as follows

\[
\mu = 4\pi \sin \theta/\lambda .
\]

\( i(\mu) \) is called the reduced intensity function and is obtained from the suitably normalized measured X-ray scattering intensity \( I(\mu) \) by the relation

\[
i(\mu) = I(\mu)|f|^2 - 1 ,
\]

where \( |f|^2 \) is the scattering per atom in the liquid.

For obvious experimental reasons, it is not possible to obtain \( i(\mu) \) for all values of \( \mu \) from 0 to \( \infty \). The limitation at low angles, chiefly due to the presence of the direct beam, is not very serious since we can extrapolate \( I(\mu) \) to \( \mu = 0 \) by a power series fit, a method that has been known to be quite satisfactory. However, the limit on the maximum value of \( \mu \), given by

\[
\mu_{\max} = 4\pi \sin \theta_{\max}/\lambda ,
\]

is far more serious. Most experiments have a \( \mu_{\max} \) of the order of 8–15 A\(^{-1}\), while even the best experiments have not achieved anything better than 20 A\(^{-1}\). The use of such experimentally limited data in the integral transform (1) leads to spurious broadening and ripples, appropriately called termination errors, in the calculated radial distribution function. We propose in this paper a scheme for reducing these errors.

2. The negative cut-off procedure

The procedure we suggest for the reduction of termination errors is based on the strict positivity of \( g(r) \). We utilise this condition through the iteration scheme described in Fig. 1. The measured intensity function \( i(\mu) \), which is not known beyond \( \mu_{\max} \), is transformed through (1) to obtain the initial estimate of \( g(r) \). This function suffers from termination errors. In particular, instead of having the value zero for values of \( r \) less than the atomic hard-core diameter, it has large amplitude oscillations, leading to negative values of \( g(r) \). A modified \( g(r) \) is now obtained from this by replacing the negative portions by the value zero. This function is back transformed to obtain a modified intensity function \( i'(\mu) \) which differs from the original \( i(\mu) \) in two ways:

(1) \( i'(\mu) \) is slightly different from \( i(\mu) \) for \( \mu \leq \mu_{\max} \).

(2) \( i'(\mu) \) is non-zero for \( \mu > \mu_{\max} \), where \( i(\mu) \) is not available.

A new composite intensity function is now built which consists of \( i(\mu) \) for \( \mu \leq \mu_{\max} \) and \( i'(\mu) \) for \( \mu > \mu_{\max} \). This intensity function is transformed through (1) to obtain a new estimate of \( g(r) \). This function will again have termination errors, but to a lesser extent compared to the initial estimate of \( g(r) \). Once again, the negative regions are chopped off and a new \( i'(\mu) \) is obtained. This cycle of operations is iterated until it converges, when we will have a modified \( g(r) \) which is positive everywhere and which leads to the measured \( i(\mu) \) within the experimentally measured range of \( \mu \). Calculations

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† For the purposes of this paper, there is no distinction between a liquid and an amorphous solid. We therefore use only the word 'liquid' hereafter.
with model functions show that in the process of removing the negative regions of the radial distribution function, there are also beneficial effects on the other spurious features present in the initial \( g(r) \).

3. The model function

For our calculations, we needed a model \( i(\mu) \) on which we could carry out computer simulation experiments. This is not trivial because the physics of the problem demands that both \( g(r) \) and \( I(\mu) \) should be positive, which denies us the possibility of using any arbitrary positive function as a model \( g(r) \). We decided to model our intensity function on the basis of the experimental liquid krypton data of Clayton & Heaton (1961) which cannot, however, be directly used because of the ubiquitous termination errors. These data were iteratively refined to a model \( i(\mu) \) by the procedure indicated schematically in Fig. 2, which is closely related to the negative cut-off procedure discussed in the previous section. This model function, which is defined between \( \mu = 0 \) and \( 30.0 \, \text{Å}^{-1} \), and is \( \leq -1 \) everywhere, leads on transformation (using \( q_0 = 0.0175597 \) atoms/Å\(^3\)) to a \( g(r) \) which is positive everywhere and equal to 0 up to the hard core diameter of 3.3 Å. The complementary model functions \( i(\mu) \) and \( \varphi(r) \) \( [= q_0 g(r)] \) are plotted in Figs. 3 and 4(a).

4. Model calculations with the negative cut-off procedure

The negative cut-off procedure was tested by computer calculations carried out on the above model function. Fig. 4 shows some of the results obtained. Fig. 4(a) gives the ‘true’ \( \varphi(r) \) obtained from the model intensity function of Fig. 3. If the model \( i(\mu) \) is truncated at \( \mu_{\text{max}} = 5.5 \, \text{Å}^{-1} \), we obtain the \( g(r) \) shown in Fig. 4(b) which is the typical appearance of a distribution function with termination errors. The following points are to be noted:

(a) There is a large ripple at small values of \( r \), within the hard-core diameter.
(b) The first peak is reduced in height by about 10%.
(c) The first peak is shifted to a larger value of \( r \) by about 0.05 Å.

![Fig. 1. Flow chart showing the negative cut-off procedure for treating termination errors in radial distribution functions.](image1)

![Fig. 2. Flow chart showing the procedure employed for obtaining a model reduced intensity function from the data of Clayton & Heaton (1961).](image2)

![Fig. 3. The model reduced intensity function \( i(\mu) \) obtained from the data of Clayton & Heaton (1961) using the iterative procedure of Fig. 2.](image3)
(d) There is a spurious subsidiary peak at \( r \approx 5.3 \text{ Å} \).

(e) The distortions in later peaks are negligible.

Fig. 4(c) shows the \( g(r) \) obtained after carrying out 200 cycles of the present negative cut-off procedure, which took about 6 min on the IBM 360/44 computer. This function is obviously an improvement on the raw \( g(r) \) of Fig. 4(b). The ripples at low values of \( r \) have practically disappeared, the main peak has shifted back to its correct position, its height has considerably improved (by about 5%) and the spurious peak at 5.3 Å has reduced, though it has not been eliminated. The results are even better for higher values of \( \mu_{\text{max}} \). The particular value of \( \mu_{\text{max}} = 5.5 \text{ Å}^{-1} \) was chosen for illustration because the termination errors for this case are easily seen visually. This example, being possibly the worst case, indicates that the present method has some merit.

5. Comparison with other methods

A few other methods have previously been proposed to deal with termination errors.

I. The following two methods are oriented towards just identifying the true and false features in the calculated \( g(r) \):

(a) Different \( g(r) \) functions are evaluated for different values of \( \mu_{\text{max}} \) on the same experimental intensity data. The false features would show much greater changes than the true ones and can hence be identified.

(b) The ripples which lead to spurious peaks are removed by multiplying the intensity function with a modifying function such as an artificial temperature factor exp \((-\alpha q^2)\). However, the true peaks would also be altered to varying degrees.

II. The following two methods attempt to obtain the whole undistorted distribution function and are hence similar in spirit to the method suggested in this paper:

(a) The method of Kaplow, Strong & Averbach (1965) uses the fact that \( g(r) = 0 \) for values of \( r \) less than the hard core diameter \( (r_c) \) and so they follow an iteration scheme essentially similar to the one shown in Fig. 2, except that at each cycle they replace the oscillating calculated function \( r_0 \left[ g(r) - 1 \right] \) by a straight line for values of \( r \) less than \( r_c \). They also initially remove the 'obvious' false features in \( g(r) \), which are identified by method I(a).

(b) The method of Enderby and co-workers (Hawker, Home & Enderby, 1974) is practically the same except that they initially identify the false features by method I(b).

In our method, we have avoided the initial removal of the 'obvious' false features since we feel that this is an unwarranted interference which could easily be biased. If, however, there is a genuine need to carry out this step, it could be easily introduced.

Our method compares favourably with methods II(a) and (b) as shown by the following discussion:

(i) Both the other methods require a knowledge of the hard-core diameter \( r_c \), within which the function \( r_0 \left[ g(r) - 1 \right] \) is fitted to a straight line. We have carried out computer experiments with these other methods (leaving out the initial step of removing the false features) for different values of \( r_c \) using the model \( i(\mu) \) of Fig. 3. When \( r_c \) was taken to be the correct value of 3.3 Å, we obtained identical results to Fig. 4(c). When \( r_c \) was taken greater than 3.3 Å the results were understandably quite bad, particularly in the region of the main peak. Rather surprisingly, the results were not very good even when \( r_c \) was taken smaller than 3.3 Å, as shown by Fig. 4(d) which illustrates the case \( r_c = 3.0 \text{ Å} \). In this figure, there is a residual ripple between 3.0 and 3.3 Å, the main peak is slightly shifted and the spurious peak at 5.3 Å is fairly strong. Since our method does not require a knowledge of \( r_c \), this may be considered a distinct advantage.

(ii) In the case of molecular liquids, the first peak in \( g(r) \) occurs at very small values of \( r \), say 1.0 to 1.5 Å, because of intramolecular vectors. In such cases, methods II(a) and (b) may not be very effective since the range of \( r \) over which \( r_0 \left[ g(r) - 1 \right] \) can be expected to be linear is very small. Our method should have no problems.

(iii) In terms of convergence, our method is surprisingly quite competitive and, in many cases, even marginally faster than the other methods. In any case, the speed of convergence is not very significant because of the availability of the Fast Fourier Transform algorithm (Cooley & Tukey, 1965).

Based on the above discussion, we feel that the new method we have presented here to deal with termination errors is a viable alternative to those already available.

6. Positivity in other fields

The only information used in the current method is the positivity of \( g(r) \). This might appear, at first sight, to be a very weak constraint and hence unlikely to lead to significant gains. However, we point out that positivity has been used with some success in similar problems in
other fields like radio astronomy* (e.g. Schell, 1965; Biraud, 1969). Also, the ‘Maximum Entropy Method’ of spectral analysis (Burg, 1975; Ables, 1974) has recently been shown by Komesaroff & Lerche (1978) to be intimately related to the positivity constraint.

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References

* The present investigation was undertaken when our attention was drawn to this work.