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Van Hove correlation functions from coherent neutron inelastic scattering

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Abstract. Experimentally determined coherent dynamic scattering functions for liquid bismuth and lead are used to derive the van Hove correlation functions $G(r, t)$ and $G_s(r, t)$. It is demonstrated that it is possible to obtain direct and physically adequate information on the atomic self-motion from a neutron inelastic scattering measurement on a completely coherent scatterer.

Since the advent of the neutron inelastic scattering technique very few attempts to derive the intermediate scattering function $F(Q, t)$ or the van Hove correlation function $G(r, t)$ from a measured dynamic scattering function $S(Q, \omega)$ have been made. There are a number of reasons of technical nature that make this procedure complicated, one of which is the difficulty in measuring $S(Q, \omega)$ for so large energy transfers that truncation errors have a negligible influence on the shape of the calculated $F(Q, t)$. The feasibility of the procedure was first demonstrated by Brockhouse and Pope (1959) who derived $G(r, t)$ for liquid lead. However, both the higher neutron fluxes available today and large improvements in the efficiency of data correction procedures have since then continuously resulted in data of much higher quality. The first reliable determination of $F(Q, t)$ for a monatomic liquid was presented by Copley and Rowe (1974). Later, Mountain (1977) used the results of Sköld *et al* (1972) to discuss the same quantity for liquid argon.

Recently Dahlborg *et al* (1985) derived $F(Q, t)$ from measured $S(Q, \omega)$ for liquid bismuth at 578 K (Dahlborg and Olsson 1982, 1983) and liquid lead at 613 K (Söderström 1981) using the extrapolation procedure to large energy transfers which was first used by Copley and Rowe (1974) for liquid rubidium. The procedure involves a fit of a sum of three Gaussian functions with ω -dependent parameters to the measured part of $S(Q, \omega)$ at constant Q -values. No physical significance, however, is attached to the choice of Gaussian functions to represent $S(Q, \omega)$ as distinct from the three Lorentzian fits used by the Delft group in their work on condensed inert gases (de Graaf (1989) and references therein). The dynamic scattering functions obtained through this fitting procedure are displayed in figure 1. The high quality of the data can be inferred from the smoothness of the three-dimensional surfaces in the ω -direction. It is gratifying to note the special characteristic features of $S(Q, \omega)$, for example, the very pronounced shoulder on the high- Q side of the main peak and the distorted second peak of $S(Q)$ for

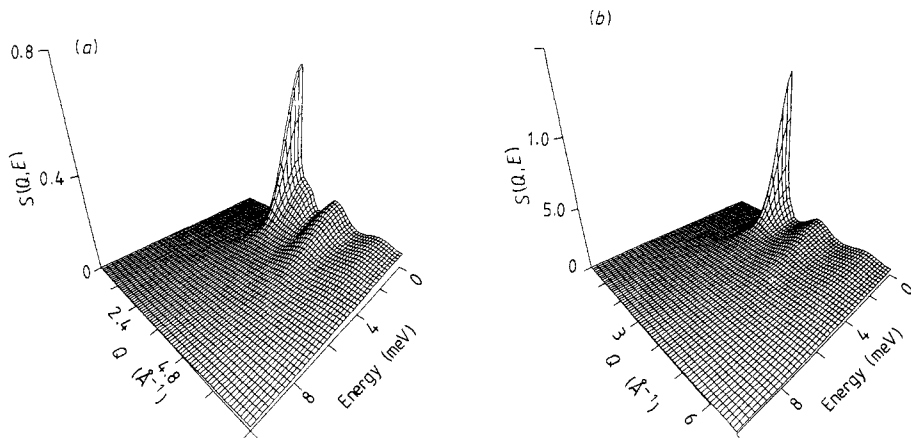


Figure 1. Three-dimensional plot of $S(Q, \omega)$ for (a) liquid bismuth at 578 K, and (b) liquid lead at 613 K.

bismuth, are clearly visible. It was further shown that the results on $F(Q, t)$ obtained by use of the fitting procedure were actually smoothed versions of directly Fourier-transformed $S(Q, \omega)$ data and it is in this context justified to consider the results shown in figure 1 as experimental, especially as the zeroth and the second energy-moments of the fitted $S(Q, \omega)$ were very well satisfied. Also, the fourth energy-moment had very reasonable values from a physical point of view. Thus, it was concluded that the data were accurate enough to allow a more in-depth analysis and the derived $F(Q, t)$ were subsequently used to obtain various memory functions (Söderström *et al* 1985, Larsson and Gudowski 1986) of great interest for comparison with modern kinetic theories and with molecular dynamics (MD) simulations. A further step in the data analysis is taken here in that the van Hove correlation functions $G(r, t)$ and $G_s(r, t)$ are derived from $F(Q, t)$.

The intermediate scattering function $F(Q, t)$ is related to the dynamic scattering function $S(Q, \omega)$ obtained in a neutron inelastic scattering experiment on a monatomic liquid by

$$F(Q, t) = \int d\omega \exp(i\omega t) S(Q, \omega). \quad (1)$$

Because of the simple analytical nature of the functions used to approximate $S(Q, \omega)$, $F(Q, t)$ can be determined directly by use of equation (1). As an example of the shape of $F(Q, t)$, its Q -dependence at $t = 0.2$ ps is shown in figure 2. It should be noted that, irrespective of large difference in shape of the static structure factor $S(Q)$ ($= F(Q, t = 0)$) in liquid bismuth and lead, there is no significant difference in the decay of $F(Q, t)$ either with time or with Q , which indicates that the structural relaxation in a liquid metal to a large degree is independent of the actual structure both with respect to space and time.

The van Hove correlation function $G(r, t)$, which can be naturally divided in two parts, a self part $G_s(r, t)$ and a distinct part $G_d(r, t)$, is obtained from $F(Q, t)$ through

$$G(r, t) = G_s(r, t) + G_d(r, t) = \frac{1}{(2\pi)^3} \int dQ \exp(iQR) F(Q, t). \quad (2)$$

Since the range of Q encompassed by the experimental results is limited ($S(Q, \omega)$ for

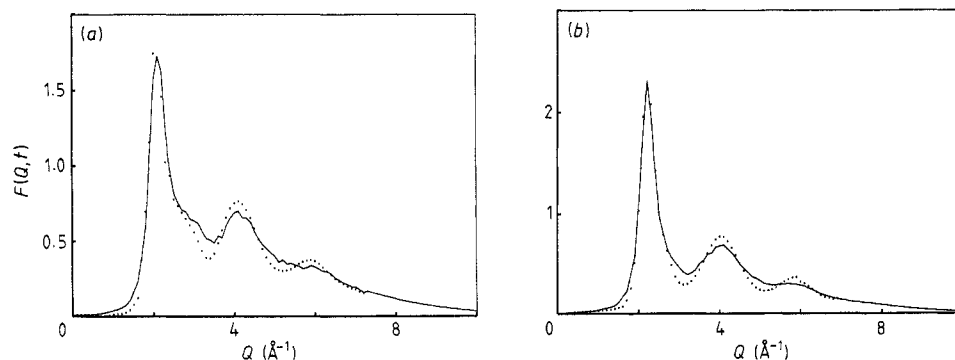


Figure 2. Derived $F(Q, t)$ for (a) liquid bismuth, and (b) liquid lead as functions of Q for $t = 0.2$ ps. The points represent the experimental results and the full curve is a fit according to equation (3).

bismuth was measured over $0.6 < Q < 7.2 \text{ \AA}^{-1}$ and for lead over $1.0 < Q < 6.8 \text{ \AA}^{-1}$, it is obvious that, in order to perform the Fourier transfer, an extrapolation of the experimental data have to be made for times shorter than 0.5 ps and for large Q (cf figure 2). At times beyond about 0.5 ps $F(Q, t)$ has essentially decayed to zero within the measured Q -region. For small Q experimental data are also missing, but the contribution from this region to the Fourier transform is very small.

From an inspection of the Q -dependence of the measured $F(Q, t)$ it was found that a suitable expression for the extrapolation to large Q was

$$F(Q, t) = F(Q, t = 0) \exp(-w(t)Q^2) \quad (3)$$

where $w(t)$ can be interpreted as a time-dependent width function. If the exponential term in equation (3) is identified with the self part of the intermediate scattering function $F_s(Q, t)$, the relation in equation (3) is identical to an earlier proposed scaling method to relate the coherent and the incoherent scattering functions (Rahman 1972). It should be emphasised that equation (3) violates the second sum rule of $S(Q, \omega)$. However, in the short-time limit where $w(t) = 0$, the assumption is trivial and it is used here at short times for the purpose of extrapolation only and no physical significance is attached to it. It should also be mentioned that different analytical forms with no physical significance for the extrapolation of Q were tried, for example, an exponential decay. The difference in calculated $G(r, t)$ functions was very small. A fitting of equation (3) to the $F(Q, t)$ curves through the method of least squares results in the full curves in figure 2. It is seen that the calculated data do not describe the experimental results in detail but that the main features of the measured $F(Q, t)$ are certainly well reproduced. As the oscillations in $F(Q, t)$ have been almost completely damped out at the highest measured Q , the exact shape of the extrapolated part has no substantial impact on the detailed shape of the derived $G(r, t)$ except at times shorter than about 0.1 ps. Because of the limited energy range of the measured $S(Q, \omega)$, the assumption in equation (3) then merely adds to the uncertainty obtained by extrapolating the measured data to infinite neutron energy transfers.

The obtained values of $w(t)$ are shown in figure 3. The first interesting feature is that the experimental points at short times very closely follow free-particle behaviour. The results from a MD simulation of Dzугutov (1989) and Dzугutov and Dahlborg (1989) also describe the experimental data reasonably well. In the MD simulation effective pair

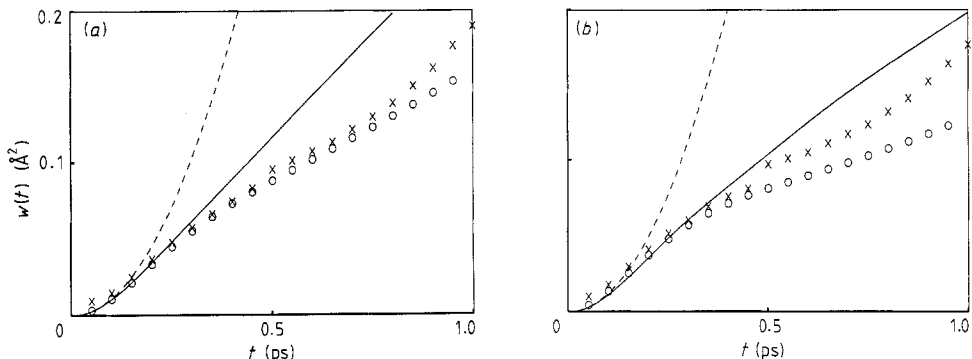


Figure 3. The width function $w(t)$ (open circles) for (a) bismuth, and (b) lead. The full curves correspond to the MD results of Dzугutov 1989 and to Dzугutov and Dahlborg (1989) and the broken curves to $w(t)$ for a free atom. The crosses are the short-time results derived from $G_s(r, t)$ shown in full in figure 5.

potentials obtained via a fitting procedure to a measured $S(Q)$ was used. The MD results shown in figure 3 were subsequently obtained from the mean-square displacement curves. It is thus expected, and was also actually shown by Dzугutov and Dahlborg (1989), that the MD simulated $S(Q, \omega)$ describe the experimentally measured $S(Q, \omega)$ very well. From a comparison of the experiment and the MD simulation it can be concluded that the approximative form for $F(Q, t)$ given in equation (3) can be used up to about 0.3 ps. Further discussion of the two different experimental data sets will be dealt with later.

Some van Hove correlation functions at a number of selected time values, calculated numerically in accordance with equation (2) and for short times with the assumption given in equation (3) are shown in figure 4, for both liquid bismuth and lead. It should be pointed out that, contrary to the case in diffraction work, the integrand in the Fourier transform decays to zero within the measured Q -range, a fact which implies that the results for small r is also trustworthy in this case. The most obvious feature of the derived $G(r, t)$, namely its two-component nature where the self-part $G_s(r, t)$ centred around $r = 0$ and the distinct part $G_d(r, t)$ which for $t = 0$ is identical the pair distribution function $g(r)$ is accordingly definitely reliable. Both $G(r, t)$ components decay with time in the expected way. It has to be stressed in this connection that the experimental points in figure 4 have been calculated from the measured dynamic scattering function $S(Q, \omega)$ for a completely coherent scatterer. This is the first time it has proven to be practically feasible to derive, to a reasonable degree of accuracy $G(r, t)$ and, especially $G_s(r, t)$ from such a measurement. It should though in this context be mentioned that neutron polarisation analysis can be used to separate $S(Q, \omega)$ and $S_s(Q, \omega)$. This has recently been demonstrated for liquid sodium (Schärpf 1989). Concentrating first on the distinct part it is very gratifying, in view of the fact that the structure is rather slowly relaxing (compare the curves for $t = 0.2$ and $t = 0.4$ ps), to note that $G_d(r, t = 0.2)$ has a shape which very closely resembles the curves obtained from a direct spatial Fourier transformation of the measured $S(Q)$ both for bismuth (Dahlborg and Davidovic 1986) and for lead (Dahlborg *et al* 1977). It can thus be concluded that neutron diffraction measurements that yield $S(Q)$ and the inelastic ones that give $S(Q, \omega)$ form a consistent set of information both for bismuth and lead. From figure 4 it is obvious that at short times there is a pronounced difference in shape between $G_d(r, t)$ for bismuth and for

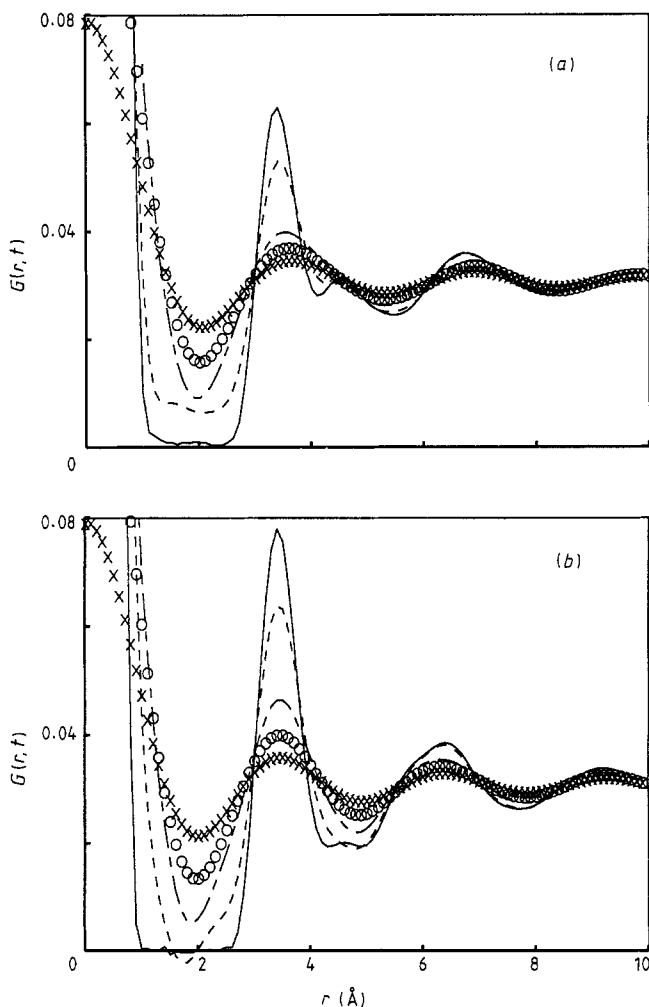


Figure 4. The shape of the pair correlation function $G(r, t)$ for (a) bismuth, and (b) lead at different times. Full curves, $t = 0.2$ ps; broken curve, $t = 0.4$ ps; chain curve, $t = 1.0$ ps; open circles, $t = 1.5$ ps; crosses, $t = 2.0$ ps.

lead. For bismuth a small but distinct subsidiary peak in $G(r, t)$ at about 4.5 \AA is visible. A similar peak has been found in other liquid semi-metals and it has been considered as a characteristic feature of $g(r)$ for this type of liquid. There is also a slight indication that such a feature exists in lead. This actually agrees with earlier findings (Dahlborg *et al* 1977).

Turning to $G_s(r, t)$, it is known that the full width at half maximum is a measure of the time evolution of the position of a single atom and as such it is a fundamental quantity in the theory of liquids. Even if the two components of $G(r, t)$ (as shown in figure 4) are merging together at long times, they can be separated unambiguously and the atomic mean square displacement (MSD) obtained from the width of $G_s(r, t)$ is shown in figure 5. The MD results of Dzugutov (1989) and Dzugutov and Dahlborg (1989) are also included. It is seen that the two sets of data agree satisfactorily at short and long times, somewhat

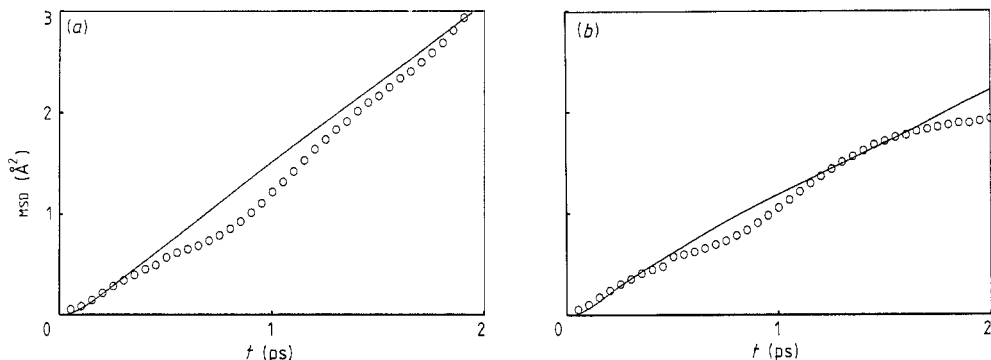


Figure 5. The mean square displacement (MSD) of an atom derived from the width of $G_s(r, t)$ for (a) bismuth, and (b) lead. The full curves correspond to the MD results of Dzугutov (1989) and Dzугutov and Dahlborg (1989).

better for bismuth than for lead. For bismuth it is actually possible to derive from the slope of the experimental data at long times a self-diffusion coefficient that agrees very well with the values obtained both from macroscopic measurements and from the MD simulation. This is the first time this has been demonstrated. At intermediate times there is a significant discrepancy between the experimental and MD data. One possible reason for this is the relatively poor correction for the experimental resolution performed by Dahlborg *et al* (1985). A simple Gaussian function was assumed to describe the resolution and this assumption is not good enough in the medium energy region of $S(Q, \omega)$ where the shape of the tail of the resolution function has a significant impact on the transformed functions. There are more accurate ways to deconvolute the experimental resolution, for example using the routes advised by Verkerk (1982) and Philip and Söderström (1985). The present results clearly indicate that these routes have unfortunately to be taken at the expense of a much more complicated numerical analysis. It should, however, also be mentioned that in many cases there is a clear difference between the experimentally obtained and MD simulated $S(Q, \omega)$ at intermediate neutron energy transfers (Copley and Rowe 1974, Kinell *et al* 1985, Dzугutov and Dahlborg 1989) well outside the limits of error given for both. The reason for this discrepancy is unknown at present.

The short-time part of the results on the atomic mean square displacement shown in figure 5 is also included in figure 3 in order to facilitate a comparison with the width function $w(t)$ obtained from the fitting of equation (3) to the experimental data. The agreement between the two sets of data up to at least 0.5 ps is striking. It is thus of fundamental interest to study whether $G_s(r, t)$ has a Gaussian shape or not. A convenient way for this is to investigate the product of the maximum value of $G_s(r, t)$ and its width at half maximum. If $G_s(r, t)$ is Gaussian, the value of the product should be equal to 0.47. As is seen in figure 6 the obtained results are both for bismuth and for lead very close to this value. At very short times the data, however, fall considerably above 0.47 indicating that, especially for liquid lead, the extrapolation procedures used in the data treatment are not entirely accurate in this time region. For longer times there is a systematic variation in the data and it can be concluded that $G_s(r, t)$ is Gaussian in shape for times shorter than about 0.4 ps and for times longer than about 1.3 ps. The time region where the most non-Gaussian behaviour is seen in figure 6 agrees well with the recent MD simulations on another liquid metal, sodium (Kinell *et al* 1985, 1989) and also agrees reasonably well with the time limits obtained by Sköld *et al* (1972) on liquid argon.

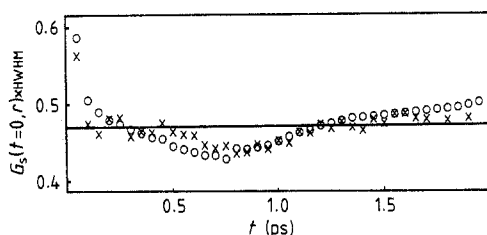


Figure 6. The width of the self-part of the correlation function at half maximum (HWHM) multiplied by its maximum value ($G_s(r=0, t)$) for bismuth (crosses) and lead (open circles) as functions of time.

In this connection, however, it should be noted that even if the overall agreement between the results on $S(Q, \omega)$ from neutron scattering and from MD simulation for liquid argon was very good there was a significant difference with regard to the time region of the non-Gaussian behaviour of $S_s(Q, \omega)$.

To conclude, it has been demonstrated above that it is possible to achieve fundamental and physically adequate information both about the distinct motion of atoms and about their self-motion from a carefully performed experiment on completely coherent scatterers. The information was obtained directly in the form of van Hove correlation functions $G(r, t)$ and $G_s(r, t)$ and without the use of any models. This model-independent treatment is of great importance and certainly increases the value of the results. Some assumptions and approximations were nevertheless used during the numerical treatment, the most important being the fit of a sum of three Gaussian functions to the measured $S(Q, \omega)$, but they have been found not to have any substantial impact on the magnitude or on the shape of the derived correlation functions.

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