

Temperature-dependent next neighbour dynamics in liquid lead

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Abstract. The temperature dependence of the density correlation function at next neighbour distances has been investigated for the liquid metal lead. This correlation function is a sensitive parameter for changes in the local environment and its Fourier transform was measured in a coherent inelastic neutron scattering experiment. The zero frequency amplitude related to the long time decay of density fluctuations decreases in a nonlinear way and indicates a change in dynamics around $1.5 \cdot T_{melt}$. The derived generalized longitudinal viscosity shows a decrease near this temperature. From these observations we suppose that solidification sets in on a microscopic level distinct above the melting point.

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1. Introduction

For a long time liquid metals have attracted researchers with different interests. On the one hand there is technological interest in understanding the solidification process in detail, which could have a large economic impact, e.g. for casting. On the other hand there is growing interest from basic research in understanding the solidification of liquids on an atomistic level, using liquid metals as model systems. As one such model system alkali metals are often investigated due to their simpler potential compared with more technological relevant metals like e.g. nickel. Around the structure factor maximum the dynamics shows a slowing down and a concomitant reduction of the line width in the dynamic structure factor, well known as deGennes narrowing [1]. In a simple picture the movement of a particle to the next neighbour position in a dense fluid is hindered and needs a rearrangement of the surrounding particles, which results in a slowing down of the relaxation process at this momentum transfer. On this length scale the dynamics is very sensitive to changes on the local environment. Recently, we measured the temperature dependence of the line width at the structure factor maximum of the alkali metal rubidium [2]. The derived amplitude at energy transfer zero shows a slope changing with increasing temperature. Because $S(Q, \omega = 0)$ is related in the time domain with long time correlations one can conclude that the decay of long time correlations changes at about 450 K ($T_{melt} = 313$ K). In addition, the derived Q-dependent longitudinal viscosity shows a decrease around 400 – 450 K with increasing temperature. This might be interpreted as the liquid metal behaving more solid-like on cooling starting at a temperature $T \approx 1.5 T_{melting}$.

Reichert et al. performed an x-ray structural investigation on the interface of liquid lead and silicon [3]. They derived a fivefold symmetry in their scattering signal, which can be traced back to a fivefold local symmetry in the liquid. A reason for this observation might be the long searched for icosahedrons in liquid metals, which are believed to be the origin for the undercoolability of liquid metals [4]. Due to this seemingly strong link of solid-like structures in liquid lead we decided to investigate the dynamics at nearest neighbour distances in this metal. The Fourier transform of the time dependent next neighbour density correlation function can be measured in a coherent inelastic neutron scattering experiment. The amplitude of this scattering function provides access to the long lasting part of the density correlation function and is therefore sensitive to changes related to a more solid-like behaviour.

There is already a long history in studying liquid lead with neutrons due to its favorable scattering properties, large coherent cross section combined with negligible incoherent cross section. Early attempts to measure the collective inelastic excitations go back to the 1950s [5]. In the 1980s new inelastic studies were made on liquid lead combined with classical molecular dynamics [6, 7]. This work was mainly concentrated on inelastic excitations near the melting point and one high temperature. An early study on the quasielastic dynamics of liquid lead at the structure factor maximum was performed by Wignall and Egelstaff for three temperatures [8]. *Ab initio* methods have also been

used to describe the structural and dynamical properties of liquid lead. The bond angle distribution was described to be near to the one expected from a local icosahedral order [9]. Here we present an experimental study on the changes of the collective dynamics at the structure factor maximum Q_0 of liquid lead with rising temperature.

2. Experimental details

The coherent dynamic structure factor $S(Q, \omega)$ of liquid lead has been measured by neutron scattering. Lead is a nearly coherent scatterer with an incoherent contribution of less than 0.003 barn compared to the coherent cross section of 11.11 barn. Lead beads (99.9 % purity) were filled in a flat niobium can with a helium gas atmosphere. The niobium wall thickness was 1.7 mm and the sample thickness 3 mm, which provided a scattering power of about 12 %. The cell was sealed by a quenched gold seal. Niobium is a nearly perfect coherent scatterer and hence will not contribute to the elastic line except where Debye Scherrer lines appear. The first reflection is at $Q = 2.7 \text{ \AA}^{-1}$, which is beyond the structure factor maximum of liquid lead ($Q = 2.2 \text{ \AA}^{-1}$) and therefore will not influence the measurements. The cell was installed in a standard furnace at a 45° orientation in transmission geometry. The experiment was performed at the OSIRIS spectrometer at ISIS, UK. This instrument is an indirect time of flight backscattering spectrometer. The PG004 reflection of the pyrolytic graphite analyzer was used, which provides a useful dynamic range from -3 meV to 3 meV around the elastic line. The energy resolution deduced from a vanadium measurement was 0.095 meV. The momentum transfer resolution is about $\pm 0.05 \text{ \AA}^{-1}$. Thirteen temperatures between 613 K and 1200 K have been measured ($T_{melting}(Pb) = 600.7 \text{ K}$) and the temperature uncertainty was smaller than $\pm 1.5 \text{ K}$ during all measurements. An identical cell was used for empty cell runs.

The evaluation of the data included an empty cell subtraction with absorption correction according to Paalman and Pings [10]. Absolute calibration has been achieved by measuring a vanadium plate. Multiple scattering at the structure factor maximum is quite small compared to the first order scattering intensity at this momentum transfer vector and no attempt was made to correct for it. A calculation for a similar scatterer gave less than 1 % twice scattered neutrons at the elastic line at the structure factor maximum [2]. Within the measured grid in (Q, ω) space constant Q spectra have been obtained by searching within appropriate limits. An energy binning of 20 μeV steps was carried out. The analysis was performed at the structure factor maximum of liquid lead $Q_0 = 2.2 \text{ \AA}^{-1}$. There is no significant shift in the peak value with increasing temperature [11], hence this value was kept for all temperatures. For the data analysis we used as a model a single Lorentzian function convoluted with the resolution function. The data fit has been performed with the Modes data analysis software, based on a Bayesian data analysis procedure [12]. Included in the fit was a linear sloping background, which probably stems from higher order reflections of the graphite analyzers. An elastic line was also fitted to take into account any incompletely subtracted contributions from

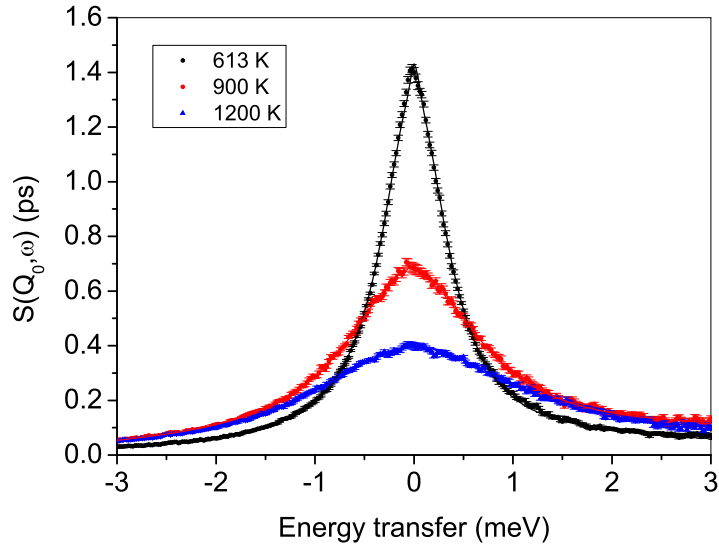


Figure 1. Three spectra are shown covering the whole temperature range. The fit is included as a line. Apparently the amplitude at $\omega = 0$ decays at temperatures up to 900 K faster than at higher temperatures.

the empty cell. From the Lorentzian description two parameters can be deduced, the line width Γ and its amplitude $S(Q, \omega = 0)$, which is connected to the area A of the Lorentzian function by $S(Q, \omega = 0) = \frac{A}{\pi\Gamma}$. In the figures, the fit errors are generally smaller than the symbol sizes.

3. Results and Discussion

Fig. 1 shows three spectra for three different temperatures. The decreasing amplitude at the elastic energy with increasing temperature is clearly visible. The amplitude decreases between 613 K and 900 K by a factor two more than between 900 K and 1200 K. This change already indicates a change in the dynamics with temperature. Fig. 2 depicts the full width at half maximum (FWHM) for the data set near the melting point. It clearly shows the so called deGennes narrowing at the structure factor maximum. Also included in the figure is the derived $S(Q)$ values from a numerical integration from -3 meV to + 3 meV. The minimum of the line width seems to be quite near to the maximum of the structure factor, although the Q -resolution is not appropriate to claim more subtle differences. A small shift between minimum in the width and maximum in $S(Q)$ was observed by P. Egelstaff et al in their earlier measurements [13].

In the following we will discuss the temperature dependence of the two fit parameters: the width and the height of the Lorentzian curve. The FWHM from the fits is shown in Fig. 3. The temperature dependence is nearly linear and there is no evidence for a significant changing slope in this temperature range, which could be a hint for a

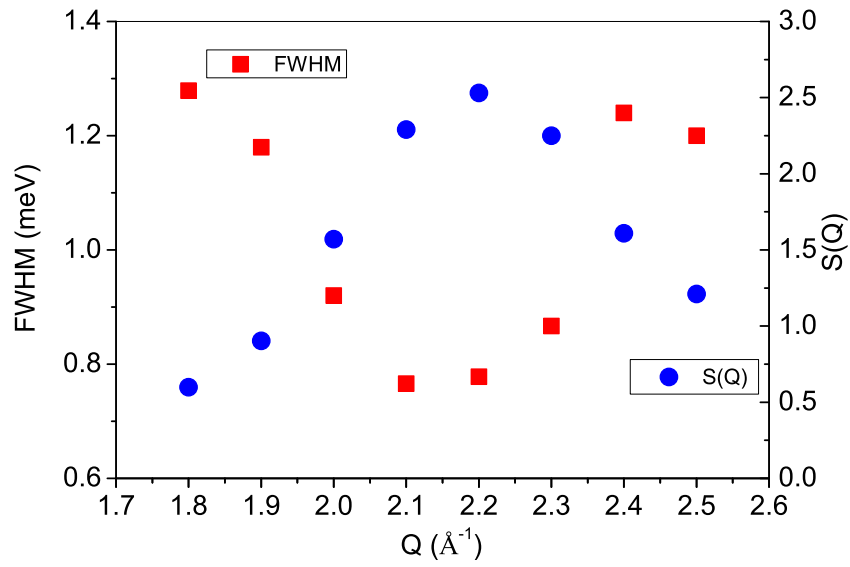


Figure 2. The Q-dependent FWHM of the data at 613 K (squares). Included are also the numerical integrated structure factor $S(Q)$ values (circles).

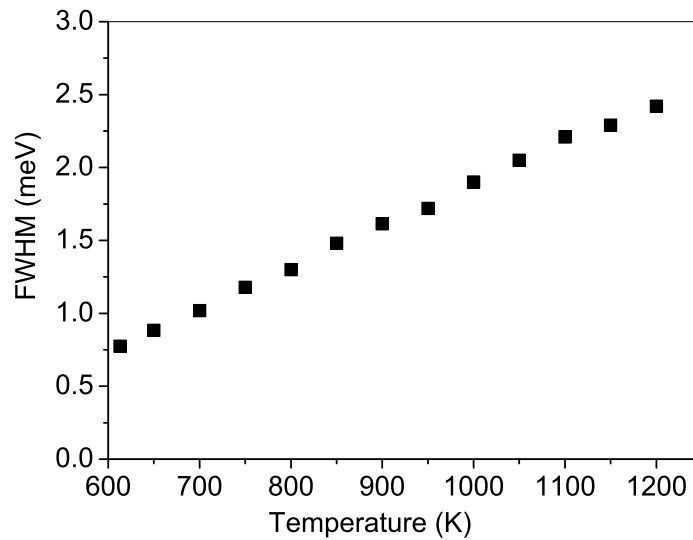


Figure 3. The temperature dependent FWHM of the data. A nearly linear increase over the whole range can be observed.

change in dynamics. The values obtained are in good agreement with earlier results on liquid lead [8]. We derive from their figure a FWHM at 640 K of about $750 \mu eV$ and we measured $775 \mu eV$. A similar agreement occurs for the high temperature value at 1000 K. At that time it was already supposed that the width at the structure factor maximum is related to a self diffusion process. Later a formal relation was derived by Cohen and coworkers [14]:

$$\omega_{1/2} = \frac{D_E Q^2 d(Q\sigma)}{S(Q)} \quad (1)$$

where $d(Q\sigma) = (1 - j_0(Q\sigma) + 2j_2(Q\sigma))^{-1}$ is given by a combination of spherical Bessel functions $j(Q\sigma)$. The hard sphere parameter $\sigma = 3.05 \text{ \AA}$ we obtained from a Percus Yevick fit to the tabulated structure factor data of Waseda [15]. Using $S(Q_0) = 2.55$ we derive, at the melting point, a diffusion coefficient of $D_E = 2.18 \cdot 10^{-5} \text{ cm}^2 \text{ s}^{-1}$. This value is in remarkable and may be fortunate agreement with the macroscopic measured diffusion coefficient [16] $D = 2.2 \cdot 10^{-5} \text{ cm}^2 \text{ s}^{-1}$. *Ab initio* simulations [9] reported for the self diffusion coefficient $D = 2.2 \cdot 10^{-5} \text{ cm}^2 \text{ s}^{-1}$. There is a well recognizable correspondence between the width at the structure factor maximum and the structure factor, which is the basis of Eq 1 (see Fig 2).

The second quantity we want to discuss is the amplitude $S(Q_0, \omega = 0)$ (see Fig. 4). Our elastic value is $S(Q_0, \omega = 0) = 1.4 \text{ ps}$ at melting temperature which can be compared to the result of Söderstrom et al [6] $S(Q_0, \omega = 0) = 0.88 \text{ ps}$. At the highest temperatures we get $S(Q_0, \omega = 0) = 0.41 \text{ ps}$ compared with $S(Q_0, \omega = 0) = 0.35 \text{ ps}$ from [6]. The differences are probably due to the large difference in energy resolution which in our measurement was a factor 10-20 better. As a guide for the eye a linear fit is included for the high temperature values, which indicates a change in dynamics around 900 K. The amplitude $S(Q_0, \omega = 0)$ is related to the long time decay of the density correlation function. It seems that the long time correlations decrease from the melting point up to about 900 K much faster than at higher temperatures. Such a behaviour can already be found in the spectra shown in Fig. 1. It is tempting to link the changing slope for the amplitudes on cooling with a more solid-like behaviour in the liquid around this temperature, which is about $1.5 \cdot T_{melt}$. The amplitude $S(Q, \omega = 0)$ is connected to the Q-dependent longitudinal viscosity coefficient $\eta_l(Q)$ according to [17, 18]:

$$\eta_l(Q) = \pi \rho v_0^2 \frac{S(Q, 0)}{S(Q)^2} \quad (2)$$

with v_0 the thermal velocity and ρ the mass density. The generalized viscosity $\eta_l(Q)$ is the zero frequency limit of the Q-dependent stress autocorrelation function [19]. In this sense the longitudinal viscosity can be regarded as being sensitive to long lasting atomic-level stress correlations, in our case, on next neighbour distances. In Eq 2 the amplitude is linked with three parameters, which are also temperature dependent: the square of the thermal velocity increases linearly with temperature, the mass density decreases nonlinearly with temperature [20] and the structure factor $S(Q)$ does the same. A more difficult parameter to get is the temperature dependent values for $S(Q_0)$. In

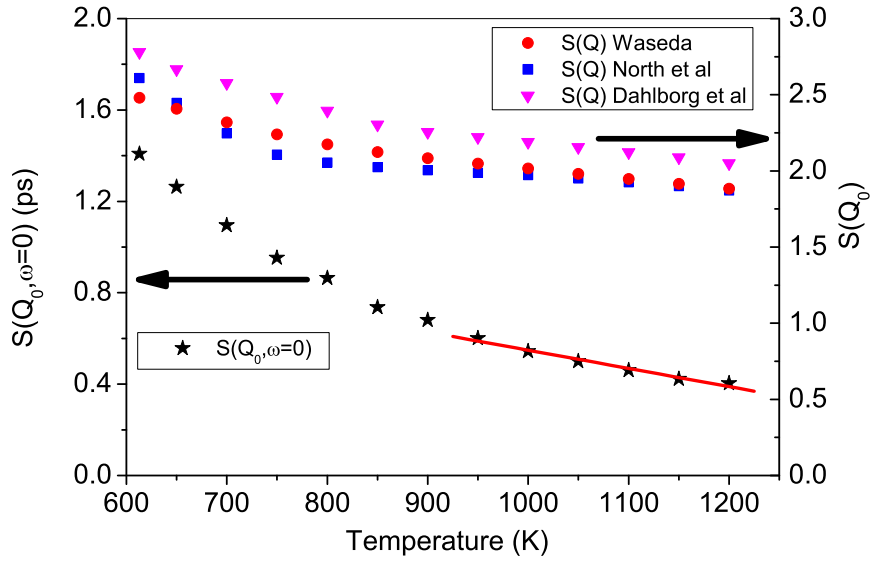


Figure 4. The amplitudes $S(Q_0, \omega = 0)$ (stars) are shown. A linear fit for the high temperature part is included as a guide for the eye. Interpolated structure factors for liquid lead from three different measurements [11, 15, 21] are included.

the literature we found three structure factor measurements for liquid lead, which cover the whole temperature range [11, 15, 21]. For all three measurements four temperature values are available over the whole range we explored. Then we interpolated $S(Q_0)$ for all our measured temperatures, which are included into Fig 4. The slightly different absolute values could be related to different Q -resolutions for the different experiments performed. In addition there is also a slightly different evolution with temperature. Using all three sets of structure factors we calculated the generalized longitudinal viscosity depicted in Fig. 5. The error bars are deduced from the $S(Q)$ uncertainty and we used ± 0.05 as the error [11]. Due to the larger $S(Q)$ values of Dahlborg et al this curve is shifted to lower values. A common result is that the generalized viscosity increases around 900 K for decreasing temperatures. Nevertheless, due to the different temperature dependence of $S(Q_0)$ at lower temperatures one viscosity curve shows a surprising behaviour. With the data of North et al the viscosity exhibits a maximum around 800 K and decreases towards the melting temperature, whereas with both other data sets it increases to a plateau-like level. Whether there is a peculiar temperature dependence of the generalized viscosity in the lower temperature range beyond an increase with decreasing the temperature would need a new more-detailed experimental study of the structure factor. From ultrasound measurements on liquid lead an increase of a factor three in the bulk viscosity up to about 900 K was deduced [22]. The bulk viscosity η_B is linked with the longitudinal viscosity η_l in the hydrodynamic case by: $\eta_l = 4/3\eta_s + \eta_B$. This might provide an indication of where to look for an

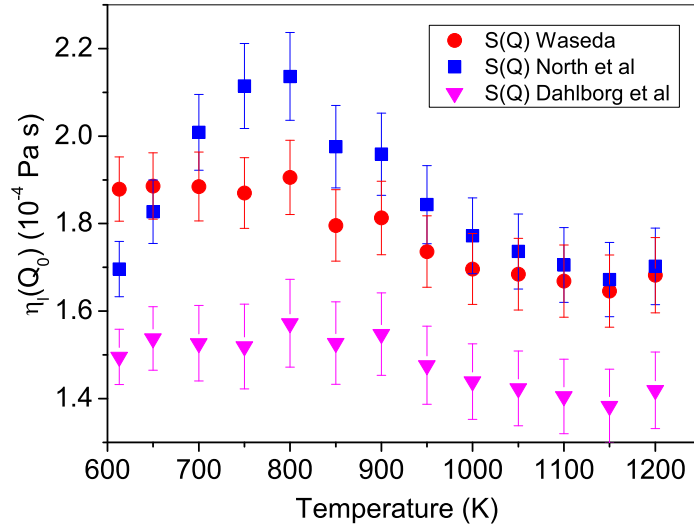


Figure 5. The generalized longitudinal viscosity at the structure factor maximum is shown derived from the amplitude $S(Q, \omega = 0)$. Values from three different measurements for the structure factor have been used.

explanation of this strange behaviour, but with a note of caution, because it has been shown that this relation breaks down at larger Q-vectors [23].

We observe the zero frequency value of the viscosity, hence this increase is related to long time correlations of the stress. The increase of stress correlations could be a sign that solidification on the atomic scale is beginning. The comparison of the different temperature dependence of the FWHM (Fig 3) and $S(Q, \omega = 0)$ (Fig 4) makes a comment necessary, because for a single Lorentzian the half width and peak height are interrelated as mentioned above. Obviously, only in the long time correlation $S(Q, \omega = 0)$ the slow next-neighbour dynamics is observed, as opposed to the FWHM, which incorporates the usual deGennes narrowing on a shorter time scale. Hence there must be an additional slow relaxation process on a longer time scale setting in on cooling the liquid below about $1.5 \cdot T_m$. This process is supposed to act as a microscopic precursor to bulk solidification. In liquid rubidium a slow relaxation process was recently observed by neutron spin echo techniques [24]. Molecular dynamics simulations predicted a distinct slowing down of this process in the supercooled region and it is supposed to be the origin for structural freezing, which eventually leads to the glass transition [25]. An interesting point for the future will be to identify this slow process in the dynamics of liquid lead.

4. Conclusion

For liquid lead the coherent structure factor $S(Q, \omega)$ has been measured by inelastic neutron scattering at the structure factor maximum. Temperatures up to twice the melting point have been recorded and evaluated. With increasing temperature, changes in the spectra have been analyzed with two parameters: the width and the amplitude of the quasielastic line. The amplitude $S(Q_0, \omega = 0)$, associated with the decay of density fluctuations on a long time scale, decreases in a nonlinear manner indicating a change in dynamics at about $1.5 \cdot T_{melt}$. The derived generalized longitudinal viscosity $\eta_l(Q_0)$, which is interrelated to local atomic stress correlations, shows a decrease around this temperature. All experimental findings indicate a more solid-like behaviour in the liquid state which sets in on decreasing the temperature from about $1.5 \cdot T_{melt}$. A similar conclusion has been drawn from studies on liquid rubidium. This raises the question whether there is a universal temperature range around $1.5 \cdot T_{melt}$, where solidification sets in for liquid metals on an atomistic level.

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