Single and collective particle dynamics in liquid \( \text{Rb}_{80}(\text{RbBr})_{20} \)

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Abstract. The temperature \((T)\) dependence of the single and the collective particle dynamics of a melt containing 80 at% Rb and 20 at% RbBr was investigated using neutron inelastic scattering. Compared to pure liquid Rb, the dispersions obtained from the maxima of the longitudinal current correlation function clearly reflect the change of the atomic interaction from a metallic to a dominantly ionic regime. The \(T\) dependence of the atomic dynamics in \( \text{Rb}_{80}(\text{RbBr})_{20} \) is characterized by a broadening of the spectra resulting in a shift to higher energies in the dispersion and in the spectrum of the velocity auto-correlation function, which was determined here for a mixture of a liquid metal with a molten salt for the first time.

1. Introduction

The mixtures of liquid metals and molten salts have attracted much interest, amongst others from a technological point of view. In these liquids, the type of interatomic interaction depends on the relative concentration of the components, similar to other so called 'liquids with competing interactions' \([1,2]\). As has been shown via the measured partial static structure factors \([3]\), mixtures of molten salts with liquid metals show a transition from a dominant metallic interaction at salt concentrations below 10 to (maximum) 15 at\% to charge ordering, i.e. an ionic interaction already at a salt concentration of 20 at\%. The dominant interaction in liquid \( \text{Rb}_{80}(\text{RbBr})_{20} \) is therefore ionic and the interest of this investigation is in the single particle dynamics as reflected by the spectrum of the velocity auto-correlation function and in the collective atomic dynamics obtained from the longitudinal current correlation function.

Theoretical investigations predict an interesting interaction between acoustic and optic type of excitations in mixtures of liquid metals and molten salts \([4,5]\), motivating part of these experimental investigations. Using triple axis spectrometry in neutron inelastic scattering, the collective dynamics of different mixtures of Rb with RbBr had been investigated before with rather different results \([6,7]\). These different results motivated us to study the temperature dependence of the atomic dynamics in \( \text{Rb}_{80}(\text{RbBr})_{20} \) using time-of-flight spectroscopy. A report on preliminary results for the collective dynamics had been given before \([8]\).

2. Experiment and data treatment

The experiments were made at the time-focusing cold neutron time-of-flight spectrometer IN6 at the High Flux Reactor of the Institut Laue-Langevin in Grenoble with an incident energy of
4.75 meV. Scattering angles between 11 and 113 degrees were used. The samples were enclosed in tight electron beam welded Nb cylinders with a wall thickness of 0.15 mm. Rb$_{80}$(RbBr)$_{20}$ was measured at 966 and at 1160K. Besides the sample an empty Nb container of the same geometry was measured at the same temperatures as the samples. The Vanadium calibration runs were done at 297 K. From the FWHM of the elastic line in the Vanadium spectra an elastic resolution of 0.17 meV was determined. This very good resolution at zero energy transfer gets worse with increasing energy in the neutron energy gain spectra used here.

In contrast to the preliminary publication, all necessary corrections are now applied to the data, including corrections for multiply scattered neutrons in the full energy range. After the corrections, the data were transformed from $S(\Theta =\text{const.}, \omega)$ to $S(Q =\text{const.}, \omega)$, where $\Theta$ is the scattering angle, $Q$ the wave-vector transfer, $\hbar \omega$ the energy transfer in the inelastic scattering process and $S(Q, \omega)$ is the dynamic structure factor. From the latter presentation the longitudinal current correlation function, $J_l(Q, \omega)$, was calculated by

$$J_l(Q, \omega) = \left(\frac{\omega}{Q}\right)^2 S(Q, \omega).$$

Because of the multiplication with $\omega^2$, $J_l(Q, \omega)$ is a spectrum with (at least) one pronounced maximum from the position of which a dispersion is obtained. The spectra of the velocity autocorrelation function, $z(\omega)$ are determined using the Egelstaff-Schofield extrapolation method [9], which works reliably for large energy transfers down to about 3 to 5 meV [2].

3. Results

![Figure 1](image1.png)

**Figure 1.** Cuts at $Q = \text{const.}$ through the total dynamic structure factor of liquid Rb$_{80}$(RbBr)$_{20}$ measured at 966 K. The increase of $S(Q, \omega)$ towards smallest $Q$ is partly due to incoherent scattering from the mixture of the two elements and partly due to concentration fluctuations.

![Figure 2](image2.png)

**Figure 2.** Zeroth frequency moments of the total $S(Q, \omega)$ of liquid Rb$_{80}$(RbBr)$_{20}$ measured at 966 K (O, shifted by 0.5) and 1160 K (△, shifted by 1.0) compared to the respective total $S(Q)$ from [10] and to $S(Q)$ of liquid Rb determined at 1073 K [11] (lines).

The total $S(Q, \omega)$ for liquid Rb$_{80}$(RbBr)$_{20}$ measured at 966 K is shown in Fig. 1. The strong increase of $S(Q, \omega)$ towards small $Q$ is partly due to incoherent scattering from the two elements.
and partly due to the concentration fluctuations present in this metal-salt mixture. At 15 nm−1 the main peak of the dynamic (and static) structure factor is observed. The second maximum is not reached in the Q-range covered in this experiment, but the minimum between the two maxima is still visible. No peaks or shoulders appear on the smooth energy dependent spectra. In Fig. 2 the zeroth frequency moment (integration of \( S(Q, \omega) \) in Fig. 1 over energy) of the two \( S(Q, \omega) \) s are compared to the total static structure factors, \( S(Q) \), measured previously [10]. In view of the low incident energy of this experiment the agreement of the data is very satisfactory.

In Fig. 3 the dispersion branches of liquid Rb₈₀(RbBr)₂₀ at \( T = 966 \) K and 1160 K obtained from the maxima of \( J_l(Q, \omega) \) are compared to the respective dispersions of liquid Rb at 766 K (\( \bigcirc \)) and 1073 K (\( \blacklozenge \))[12]. The dispersions are shifted to higher energies with increasing \( T \). For Rb₈₀(RbBr)₂₀, the first dispersion minimum is at slightly higher \( Q \) than that of Rb and no clear second minimum is found. Finally, Fig. 4 shows the spectra of the velocity auto-correlation function of the samples determined at both temperatures. Towards higher \( T \), a transfer of modes in the normalized spectra from the low energy region below 5 meV to energies above 10 meV is observed, which is due to the broadening of the spectra on energy scale with increasing \( T \).

4. Discussion

When discussing the above results one should keep in mind that the total correlation functions and their spectra discussed here may be different from the corresponding partial correlation functions and their spectra. In case of a binary system, the total spectra are the weighted sum of three partial dynamic structure factors, \( S_{ij}(Q, \omega) \) (\( i,j = \text{Rb,Br} \)), which represent the collective dynamics, and two contributions from incoherent neutron scattering, \( S_i^{inc}(Q, \omega) \), the latter being related to the single particle motion. Thus the total \( S(Q, \omega) \) shown in Fig. 1 is the weighted sum of five partials weighted by the respective concentrations (\( c_i \)), neutron scattering lengths (\( b_i \)) and neutron incoherent scattering cross-sections (\( \sigma_i^{inc} \))

\[
\sigma S(Q, \omega) = 4\pi \sum_i \sum_j b_i b_j \sqrt{c_i c_j} S_{i,j}(Q, \omega) + \sum_i \sigma_i^{inc} c_i S_i^{inc}(Q, \omega)
\]
σ is the total effective scattering cross section. In the present case, the weighting factors 
\[ w = b_i b_j \sqrt{c_i c_j} \] favor strongly the collective dynamics (\( w = 0.925 \)) and the Rb-Rb correlations 
(\( w = 0.828 \)) or, rephrasing the partial structure factors following Bathia and Thornton, the 
number correlations reflected in \( S_{NN}(Q, \omega) \), making the observation of optic type of modes with 
neutrons in this mixture rather unlikely. The total \( S(Q, \omega) \) (see Fig.1) just shows one principal 
maximum near 15 \( \text{nm}^{-1} \) and otherwise a rather smooth energy dependence. This is the reason 
why we decided to determine the dispersions shown in Fig. 3 from the maxima in \( J_i(Q, \omega) \).

Compared to \( S(Q) \) of liquid Rb determined at 1073 K [11] the first maximum in the zeroth 
moment of the two dynamic structure factors (and in the measured \( S(Q) \) [10]) is only slightly 
shifted to larger \( Q \) and the first minimum is much shallower. This fact is very well reflected in 
the dispersion curve shown in Fig. 3. In contrast to the dispersion of liquid Rb, the dispersion 
of the mixture only shows one clear minimum, the position of which is close to the position 
of the principal peak in \( S(Q) \). Unlike for other systems [1,2], no considerable shift of the 
dispersion to higher energy transfers is observed as a function of composition at constant \( T \). For 
Rb\(_8\)(RbBr)\(_{20}\), there is no second dispersion minimum, but a change of slope of the dispersion 
in the \( Q \)-region corresponding to the first minimum of \( S(Q) \). Whether this change of slope is 
caused by the indication of a second minimum in the dispersion next to the second maximum 
of the static structure factor, not fully reached here (see Fig. 1), or from a possible interaction 
of the acoustic type of excitations shown in Fig. 3 and optic modes in this \( Q \)-region, where the 
partial structure factors due to number and to concentration correlations have approximately 
equal weight [3], is difficult to decide on the basis of the present results.

The - from the point of view of vibrations in solids - unexpected \( T \) dependence of the 
dispersions we ascribe to the broadening of the excitations with increasing \( T \), magnified even 
stronger in \( J_i(Q, \omega) \) than this would be the case in \( S(Q, \omega) \). This broadening, leading to an 
intensity transfer from the energy region below 5 meV to above 10 meV, is even more clearly 
seen in the normalized spectra of the velocity auto-correlation function, \( z(\omega) \) (Fig.4). To our 
knowledge this is the first time this function, reflecting the single particle motions, is determined 
for any liquid metal-molten salt mixture.

5. Conclusions

The change in the atomic interaction from a nearly free electron screening (metallic interaction 
as e.g. in liquid Rb) to screening by charge ordering in the dominant ionic interaction in 
Rb\(_8\)(RbBr)\(_{20}\) is reflected by clear changes in the dispersions. The increasing broadening with 
increasing \( T \) - also observed in the spectrum of the velocity auto-correlation function, \( z(\omega) \) (Fig.4). To our 
knowledge this is the first time this function, reflecting the single particle motions, is determined 
for any liquid metal-molten salt mixture.

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