Investigations of diffusion processes in liquid lithium and lithium–hydrogen melt by quasielastic neutron scattering

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Abstract. The quasielastic neutron scattering experiments on liquid lithium (at 500 K and 830 K) and lithium-hydrogen melt (99 at.% Li7 and 1 at.% H at 830 K) were performed with the DIN-2PI time-of-flight spectrometer (FLNP, JINR, Dubna). The characteristics of the diffusion mobility for particles comprising the liquids studied are extracted from the experimental results and analyzed with the help of the phenomenological and theoretical models. The self-diffusion coefficient in liquid lithium obtained for both temperatures is in the agreement with the one known in literature. The questions connected to hydrogen diffusion in the liquid lithium are discussed.

1. Introduction
The work presented is aimed to get the information about diffusion processes in pure liquid lithium and lithium–hydrogen melt. There are no doubts in practical importance of such investigations from the point of view of nuclear power engineering [1] as well as thermonuclear problems [2].

The experimental neutron scattering results on liquid lithium (T = 500 K and 830 K) and lithium–hydrogen melt (T = 830 K, hydrogen concentration ~ 1 at.%) were obtained with the DIN-2PI spectrometer (IBR-2 pulsed reactor, Frank Laboratory of Neutron Physics, JINR, Dubna) [3]. The experimental conditions were chosen with the aim to facilitate the measurements and analysis of the quasielastic scattering region. This fact, in its turn, opens the possibility to get the information about the characteristics of diffusion processes in the liquids under study. The initial neutron energy was taken to be Eo = 3.61 meV (ΔEo ~ 0.17 meV). The sample container, a cylindrical layer with the thickness of 7 mm and the height of 100 mm, was made from a niobium foil of 0.3 mm thickness by electron-beam welding. So, the coherent elastic scattering effects on the container in the region of neutron wave vector transfer Q < 3 Å⁻¹ were practically excluded.

The results of quasielastic scattering were obtained in the Q region of 0.2 Å⁻¹ to 2 Å⁻¹. Based on the Lovesey model [4] it was supposed that the coherent effects on liquid lithium in this Q region are negligible. After introduction of all the required corrections (neutron flux attenuation in the sample and the container, effects of the container, detector efficiency, multiply scattering estimated as less...
than 5% of common scattering for \( Q \approx 2 \, \text{Å}^{-1} \), the quasielastic scattering results were transformed into the equienergy scale and \( Q \)-constant representation. The examples of the incoherent quasielastic scattering peaks for a number of \( Q \) are shown in figure 1.

2. Results and discussion

2.1. Liquid lithium

The quasielastic scattering results for pure lithium were analyzed under assumption that the natural form of incoherent quasielastic scattering peaks can be described by a single Lorentzian curve:

\[
S(Q, \varepsilon) = \left( \frac{AB}{2\pi} \Delta E(Q) \right) \left( \varepsilon^2 + \frac{1}{4} \Delta E(Q)^2 \right) + (a + b\varepsilon) \right) R(Q, \varepsilon)
\]

where \( A \) is a thermal factor (in our conditions it does not influence the shape of quasielastic scattering peaks), \( B = \exp(-Q^2 <u^2>/k_B) \) is Debye-Waller (D-W) factor and the second term in (1) takes into account the effects of inelastic scattering: for \( S(Q < 2 \, \text{Å}^{-1}, 0) \) less than 5%. The sum of two terms in (1) is convoluted with the spectrometer resolution function \( R(Q, \varepsilon) \) measured on the special vanadium sample.

The \( Q \)-dependence of full natural widths at the half-maximum (FWHM) of the incoherent quasielastic scattering peaks, that we get from our experimental data for two temperatures, is presented in figure 2. The analysis of these results was performed in two steps. At the first step the experimental points of figure 2 were described by the phenomenological model [5], which supposes the mixed character of diffusion mobility in liquid. It includes two mechanisms: jump diffusion (with parameter \( \tau_o \), the residence time of a particle around the temporary equilibrium position) and continuous diffusion (with parameter \( D_o \), coefficient of continuous diffusion of a particle together with surroundings). The quasielastic peak is supposed to be a Lorentzian with FWHM:

\[
\Delta E_r = 2h / \tau_o \left[ 1 + D_o Q^2 \tau_o - \exp(-Q^2 <u^2>/k_B)/[1 + (D - D_o)Q^2\tau_o] \right]
\]

where \( D \) is a total coefficient of diffusion, \( <u^2> \) is a mean square amplitude of particle vibrations in the force field of neighbours. \( <u^2> \) was calculated with the help of the liquid lithium frequency distribution spectra, had got before [6]. Optimal fitting of the experimental points by expression (2) is shown in figure 2, with the respective parameters, given in this figure as well.

The values of self-diffusion coefficients for both temperatures are in a satisfactory agreement with the known data [7].

The second step in the analysis of the experimental results, given in figure 2, consists in the comparison of these data with the theoretical calculations. As it was repeatedly underlined in the literature (see, for instance, [8, 9]) the main features of diffusion self-dynamics of liquid particles are reflected in two characteristics of incoherent quasielastic scattering: reduced FWHM of the quasielastic peak

\[
\Delta k(Q) = \Delta E / 2hDQ^2
\]

and reduced amplitude of the quasielastic peak

\[
\Sigma(Q) = S(Q,0)2hDQ^2.
\]

The amplitude of the quasielastic peak is found from the expression

\[
S(Q,0) = P(Q) / \Delta E
\]

where \( P(Q) \) is an area of the quasielastic peak which we supposed to be equal to the D-W factor that we had obtained earlier [6]. So, the reduced amplitude of the quasielastic peak takes the form:

\[
\Sigma(Q) = S(Q,0) / 2hDQ^2 = P(Q) / \Delta k(Q).
\]
Our experimental $\Delta k(Q)$ and $\Sigma(Q)$ of liquid lithium for two temperatures are shown in figures 3 and 4, respectively.

At present for the estimation of the real $\Delta k(Q)$ and $\Sigma(Q)$ deviation from the hydrodynamic predictions (continuous diffusion) the methods of the generalized kinetic theory or mode coupling theory (MCT) are usually applied [8, 9]. One of the MCT versions is based on the assumption that slowing down of the particle diffusion mobility as compared to the hydrodynamic predictions takes place due to the interaction of particle diffusion motions with the shear modes of surroundings [10]. According to the predictions of this MCT version the real deviations of $\Delta k(Q)$ and $\Sigma(Q)$ of the incoherent quasielastic peaks depend on $Q$ linearly:

$$\Delta k(Q) = 1 - aQ, \Sigma(Q) = 1 + bQ.$$  \hspace{1cm} (7)

The calculations based on the MCT version which supposes the diffusion of the tagged particle to be influenced by the wider excitation spectrum of surroundings leads to the conclusion: the deviations of real $\Delta k(Q)$ and $\Sigma(Q)$ from hydrodynamics depend on $Q$ quadratically [11]:

$$\Delta k(Q) = 1 - aQ^2, \Sigma(Q) = 1 + bQ^2.$$  \hspace{1cm} (8)

Figures 3 and 4 show that our experimental $\Delta k(Q)$ and $\Sigma(Q)$ in the small-$Q$ region follow expression (8).

Our results in figures 3 and 4 are obtained in the restricted region of $Q$: for $T = 500$ K $Q < 2\text{Å}^{-1}$. Nevertheless, as it can be seen for larger $Q$, the results demonstrate some flattening tending to minimum (for $\Delta k$) and maximum (for $\Sigma$), which correspond to the main peak of the structure factor. It is usually understood as reflection of space dependence of diffusion processes [8].

2.2. Lithium–hydrogen melt

In the analysis of the experimental data on lithium–hydrogen melt expression (1) was used with an additional Lorentzian which hypothetically had to account for scattering on hydrogen. But we failed to describe the incoherent quasielastic peaks in the melt by superposition of two Lorentzians. The second component with the FWHM, which is remarkably different from the first one was not revealed. Moreover, the FWHM of the single Lorentzians in the melt was found to coincide the ones obtained for pure lithium (see figure 5). The similar diffusion characteristics of pure lithium and lithium–hydrogen melt give rise to the assumption: in our experimental conditions hydrogen exists and diffuses in the lithium–hydrogen melt in the form of lithium hydride, LiH. When applying expression (2) to describe the experimental points of figure 5, we got the diffusion coefficient $D_{\text{LiH}} = (24.8 \pm 1.5) \text{cm}^2/\text{s}$ for it. Within the limits of experimental errors this value agrees with that for pure lithium, therewith being slightly less than the latter, possibly because of a small difference in mass.

Our conclusions on the hydrogen diffusion in liquid lithium are akin to the ones obtained in [12], but disagree with the results presented in [13] and [14].

3. Conclusion

From the inelastic neutron scattering spectra for liquid lithium ($T = 500$ K and 830 K) and lithium–hydrogen melt ($T = 830$ K, hydrogen concentration ~ 1 at.%) the incoherent quasielastic component was extracted. The FWHM and amplitudes of the quasielastic peaks were analyzed and some characteristics of diffusion mobility in the liquids under study were revealed.

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Figure 1. Experimental peaks of incoherent quasielastic scattering on liquid lithium and their description by the Lorentzian curves for a number of $Q$, $T = 500$ K. The thin curve shows the spectrometer resolution function.

Figure 2. Natural half-width of incoherent quasielastic peaks $\Delta E(Q)$ of liquid lithium for two temperatures. The solid lines are the optimal description of the set of experimental points with model (2) with the parameters, given in the text. Dashed line shows the half-width of spectrometer resolution function.
Figure 3. Reduced natural half-width of incoherent quasielastic peaks of liquid lithium for two temperatures. The solid lines are the calculations with equations (7) and (9).

Figure 4. Reduced amplitudes of incoherent quasielastic peaks of the liquid lithium for two temperatures. The solid lines are the calculations with equations (8) and (10).

Figure 5. Natural half-width of incoherent quasielastic peaks of lithium–hydrogen melt (full points) and hydrogen admixture (open points). The solid line shows the optimal description of the set of experimental points with model (2). The dashed line represents the same for pure lithium.