Atomic dynamics of liquid lithium and lithium–hydrogen melt investigated by inelastic neutron scattering

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Abstract. From the experimental data on inelastic neutron scattering the frequency spectrum of lithium atomic vibrations is extracted at the temperature of 22, 227, 397 and 557 °C. The frequency spectrum for lithium–hydrogen melt (98 at.% Li, 2 at.% H) has been obtained at 557 °C. Based on the frequency spectrum, the temperature dependencies of the mean-square of the lithium atoms displacements in time, the mean-square amplitude of atomic vibrations, velocity autocorrelation function of atoms are calculated. A generalized frequency spectrum of hydrogen atomic vibrations in lithium–hydrogen melt is obtained.

1. Introduction
Melts of alkali metals have been repeatedly studied through a number of years by inelastic slow neutron scattering [1, 2], that gives sufficient information on microscopic dynamics of liquids. The possible use of liquid lithium as a coolant for nuclear power plants accounts for the study of the characteristic features of this metal melt at the development of the coolant technology and its purification from impurities [3]. The traditional technology deals with macroscopic properties of liquid metals, based on the phenomenological approach mainly. Further progress both in the applied area and in the liquid theory is obviously impossible without a detailed study of liquid microstructure and microdynamics.

The above stated circumstances have defined the main purpose of this study: to receive the most important microdynamic characteristics: the frequency spectrum of atomic vibrations in liquid lithium and lithium–hydrogen melt. Knowing the frequency spectrum, it is possible to obtain exhaustive information on atomic dynamics of the system under study [4, 5].

2. Experimental
Experiments on inelastic neutron scattering in liquid lithium and lithium–hydrogen system were performed with a DIN-2PI time-of-flight spectrometer [6] running from the IBR-2 pulsed reactor (Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, Dubna). The initial neutron energy $E_0$ was 30.8 meV, and the energy resolution was $\Delta E_0/E_0 \sim 10\%$. Samples of Li and Li–H melts in the form of a hollow cylinder with outer and inner diameters of 80 and 65 mm and a height of 110 mm were placed in containers made of Armco-iron foil of 0.15 mm in thickness. The use
of this material has allowed scattering from the container to be minimized at given $E_0$. Lithium consisted of isotope Li$^7$ with admixture 0.2 at.% of Li$^6$.

Measurements were performed for solid lithium at the temperature of 22°C, for liquid lithium at 227, 397 and 557°C ($T_{mp}(Li) = 180.7^\circ C$ [7]), and for Li–H melt at 557°C. The hydrogen admixture in the melt was of 2 at.%.

3. Results and discussion

To obtain double-differential neutron scattering cross sections, the measured spectra were corrected for attenuation of the scattered neutrons as a result of their transmission through the sample in the presence of the container and as a result of their transmission through the container in the presence of the sample, as well as the corrections for self-shielding of the empty container. The energy dependence of detector efficiency has been taken into account also.

![Figure 1](image1.png)  
**Figure 1.** Double-differential cross-sections of single neutron scattering for liquid lithium (open circles) and Li–H melt (full circles) at small scattering angles. $T = 557^\circ C$.  

![Figure 2](image2.png)  
**Figure 2.** Frequency spectrum of lithium atomic vibrations.

![Figure 3](image3.png)  
**Figure 3.** Temperature dependencies of the mean-square amplitude of atomic vibrations and the sound velocity in liquid lithium: points are the experimental data, the solid line represents the tabular data [7].  

![Figure 4](image4.png)  
**Figure 4.** Frequency spectrum of atomic vibrations: Li–H melt (full circles); hydrogen (open circles), and solid lithium hydride (dashed line) from reference [11].
3.1. Liquid lithium

The frequency spectrum of liquid lithium was extracted from the experimental data in two stages. At the first stage, since about 44% of lithium neutron scattering is coherent, the frequency spectrum was obtained from double-differential scattering cross sections for small scattering angles by the Oskotskiy method [8]. Herewith the experimental spectra were preliminary refined from multiphonon and multiple scattering contributions [5]. Typical double-differential cross sections of single one-phonon scattering for pure lithium and Li-H melt are shown on figure 1.

At the second stage, the frequency spectrum was obtained in the incoherent approximation. The double-differential scattering cross sections have been used for the large angles ($90^\circ < \theta < 130^\circ$), where no coherent effects can be find.

The experimental frequency spectra for solid and liquid lithium are shown at figure 2. One can see that the shape and position of the frequency spectra maximum depend only slightly on temperature. On the basis of the known relations (see, for example [9]), the frequency spectrum allows us to obtain a number of other microdynamic characteristics of substance. For liquid lithium with the use of frequency spectrum the following parameters were calculated: the time dependent mean-square atomic displacement, $G(t)$, the mean-square amplitude of atomic vibrations near the equilibrium positions, $\langle u^2 \rangle (T)$, and the velocity autocorrelation function, $\psi(t)$. The latter describes the correlation between the particle velocities at two instants. The position of the minimum of this function indicates the characteristic time of existence of an atom in the nearest-neighbor mode and makes it possible to evaluate the dominant frequency of atomic vibrations in liquid. The energy of these vibrations, $\varepsilon$, for liquid lithium is equal to $\sim 35 - 40$ meV, thus corresponding to the peak positions of the frequency spectrum.

Figure 3 shows the mean-square amplitude of lithium atomic vibrations, obtained as an asymptote of the $T(t)$ function. Within the experimental errors, the dependence $\langle u^2 \rangle (T)$ is linear. This fact indicates the absence of anharmonicity of atomic vibrations in the liquid under study. We have estimated the Debye temperature $\theta_D$ from the part of the frequency spectrum at small $\varepsilon$, and found the sound velocity in the melt using the formula from reference [10] (see figure 3). Within the experimental errors, the obtained values for sound velocity are in agreement with the literary data [7].

3.2. Lithium–hydrogen melt

Figure 1 gives ground to suppose that double-differential scattering cross sections can be considered as additive at small $\theta$: the metal (lithium) matrix determines the acoustic part, whereas protons (hydrogen) determine the optical excitation branch. In this assumption, from the difference spectra obtained by subtraction of the liquid lithium spectrum from Li–H melt spectrum the frequency spectrum of proton in Li–H melt has been obtained for the small and then averaged $\theta$ (see figure 4).

To obtain the frequency spectrum for multicomponent melt the following formula for the double-differential scattering cross section [9] should be used:

$$
\frac{d^2\sigma}{d\Omega dE} = \frac{k}{2k_0N} \frac{Q^2}{\varepsilon} \frac{\theta(\varepsilon)}{\exp^{\frac{\varepsilon}{k_BT}} - 1}.
$$

(1)

Here, $\Omega$ is a solid angle; $E$ is a scattered neutron energy; $k_0$ and $k$ are the wave-vectors of the incident and scattered neutrons, respectively; $Q$ is neutron wave vector transfer; $N$ is the number of particles in the system; $k_B$ is Boltsman constant. According to equation (1), the experimental data are used to determine not the frequency spectrum, $g(\varepsilon)$, but the neutron-weighted spectral function $\theta(\varepsilon)$:

$$
\theta(\varepsilon) = g(\varepsilon) \sum_{j=1}^{n} f_j \frac{a_{inc,j}^2}{M_j} \exp^{-2W_j} \langle C_j^2(\varepsilon) \rangle
$$

(2)

where $a_{inc,j}$ is the incoherent scattering length of atom of the $j$-th type, $P_j = \langle C_j^2(\varepsilon) \rangle$ is the mean-
square phonon polarization vectors of the melt components \( \sum_{j=1}^{n} f_j P_j = 1 \), and \( f_j \) is the relative fraction of atoms with the mass \( M_j \). Note that the spectral function (2) can be written in another form:

\[
\theta(\varepsilon) = \sum_{j=1}^{r} f_j \left( \frac{a_w^2}{M_j} \right)^2 e^{-2\omega_j} g_j(\varepsilon), \quad (3)
\]

where \( g_j(\varepsilon) \) is the partial frequency spectra of system components. Using the frequency spectra found for lithium and hydrogen, we can find, according to (3), the function \( \theta(\varepsilon) \) for Li–H melt. Now, knowing \( \theta(\varepsilon) \), we can obtain the frequency spectrum of this melt from equation (2) (see figure 4), using the polarization vectors calculated in reference [11] for solid lithium hydride LiH. It can be seen that this frequency spectrum is in general similar to that of solid LiH from [11].

4. Conclusions

From the experimental data on inelastic slow-neutron scattering the temperature dependence of the frequency spectrum of liquid lithium was obtained. The mean energy of the frequency spectrum is stated approximately constant in the observed temperature region and equals to 35 – 40 meV.

Based on the frequency spectrum, the temperature dependence of the mean-square amplitude of atomic vibrations in liquid lithium has been obtained. Its linear character indicates a small degree of anharmonicity of atomic vibrations in liquid lithium. This fact confirms the concept about liquid alkali metals (in particular, lithium) as weakly “anharmonic” liquids [4].

The generalized frequency spectrum of hydrogen atom vibrations in Li–H melt (98 at.% Li, 2 at.% H) is obtained. The mean spectral energy (~ 100 – 120 meV) significantly exceeds that for pure Li.

The frequency spectrum of atomic vibrations of Li–H melt is obtained. It is shown that its specific features are in general similar to the features of the frequency spectrum of solid LiH.

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