

# Dynamic structure factor in liquid cesium on the basis of time-scale invariance of relaxation processes

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The dynamic structure factor  $S(k, \omega)$  in liquid cesium near the melting point at  $T = 308$  K is studied by means of Zwanzig-Mori's memory function formalism. The spectra of  $S(k, \omega)$  are calculated on the basis of the idea of time-scale invariance of relaxation processes in liquid metals, which appeared on the fourth relaxation level. The obtained spectra of  $S(k, \omega)$  are compared with the results of the inelastic neutron scattering measurement. For the description of memory effects we use the statistical presentation about the non-Markovity parameter  $\varepsilon_1(k, \omega)$ . We find that collective excitations at the low wave vector values have a non-Markovian nature.

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The study of collective effects in simple liquids has been the subject of intense interest over the last few years in Inelastic Neutron Scattering (INS) experiments [1], Molecular Dynamics (MD) simulations [2, 3] and different theories [4]. According to these methods, liquid alkali metals have distinct collective excitations in a wide range of wave vector values and also outside the hydrodynamic region. This fact was obtained from the careful analysis of the dynamic structure factor  $S(k, \omega)$  spectra. High-frequency peaks are appreciable in  $S(k, \omega)$  for the low- $k$  values (approximately, up to half the position of the first maximum of the static structure factor), and these peaks do not exist in high- $k$  regions. Understanding the microscopic mechanism responsible for the propagation and the damping of these excitations is still a challenge in liquid metals, where the dynamics is conditioned by the interacting electron gas effects. So, a recent INS experiment on liquid cesium near its melting point has been done by Bodensteiner et al. at Grenoble [5]. The results of their experiment have shown that the high-frequency collective excitations exist in this system for wave vector region  $k < 1.1 \text{ \AA}^{-1}$ . MD simulation performed by Kambayashi and Kahal [2] validated fully the findings of INS in liquid cesium. The analysis of collective excitations, extending beyond the hydrodynamic limit, is a great contribution to the development of theoretical models of the liquid state [6].

For a system composed of  $N$  particles of mass  $m$ , the density fluctuation are given by

$$\rho(k, t) = N^{-1} \sum_{j=1}^N \exp[ikr_j(t)],$$

where  $r_j(t)$  is coordinate of the  $j$ -th particle,  $k$  is wave vector. Then the main dynamical quantity of interest is the density-density correlation function  $F(k, t) = \langle \rho^*(k, 0) \rho(k, t) \rangle / \langle |\rho(k, 0)|^2 \rangle$ , where  $\langle |\rho(k, t)|^2 \rangle = S(k)$  is the static structure factor. The angular brackets denote an equilibrium ensemble average at temperature  $T$  and density  $\rho = N/V$  with  $V$  the volume of the system involved. If  $F(k, t)$  is known, the dynamic structure factor follows from

$$S(k, \omega) = [S(k)/\pi] \lim_{\epsilon \rightarrow +0} \text{Re}[F(k, i\omega + \epsilon)].$$

According to the memory function (MF) formalism and the projection operator method [7], we can find the time evolution of  $F(k, t)$  in the following way:

$$\frac{dF(k, t)}{dt} = -\Omega_1^2 \int_0^t d\tau M_1(t - \tau) F(k, \tau). \quad (1)$$

Here we introduce the first general relaxation frequency parameter  $\Omega_1^2$  and the MF of the first order  $M_1(k, t)$ . However, by using the same method, we can define the time evolution of the high order MF  $M_1(k, t)$ ,  $M_2(k, t)$ , ... Thus, a set of interconnected relaxation processes corresponds to an arbitrary relaxation process (for example, to a density fluctuations in liquids), which can be easily taken into account by MF formalism.

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According to the definition, for ergodic processes the correlation functions  $M_0(k, t) = F(k, t)$ ,  $M_1(k, t), \dots, M_i(k, t)$  have the following properties:

$$\lim_{t \rightarrow 0} M_i(k, t) = 1, \quad \lim_{t \rightarrow \infty} M_i(k, t) = 0. \quad (2)$$

Thus, the correlation functions  $M_i(k, t)$  have characteristic time scales, which can generally be defined at fixed  $k$  case by equation

$$\tau_i = \text{Re}[\widetilde{M}_i(0)], \quad \widetilde{M}_i(s) = \int_0^{\infty} dt M_i(t) e^{-st}. \quad (3)$$

Here  $\text{Re}[\dots]$  denotes the real part of  $[\dots]$ .

These time scales  $\tau_i$  characterize the corresponding relaxation processes and can have different numerical values. Nonetheless, on a certain level, (for example, on the  $i$ -th level) the scale invariance of the nearest interconnected relaxation processes can exist. Physically it implies the existence of the Time-Scale Invariance (TSI) of relaxation processes on the nearest  $i$ -th and  $(i+1)$ -th relaxation levels. Such approach allows to receive approximation of the form  $M_{i+1}(k, t) \approx M_i(k, t)$ , which is actually the closure of the chain of integro-differential equations similar to 1. As a result, only the first  $(i-1)$  variables are necessary for the full description of the investigated system. In case of simple liquid metals by analogy with hydrodynamics region we propose, only three variables, namely local density, local momentum density, and local energy density sufficient to reproduce its spectral features at the microscopic level. These variables are implicitly present in  $F(k, t)$ ,  $M_1(k, t)$  and  $M_2(k, t)$ . From the above reasoning, one can write the following closure  $M_4(k, t) \approx M_3(k, t)$ . By means of Laplace transformation of the corresponding equations for  $M_0(k, t) = F(k, t)$ ,  $M_1(k, t)$ ,  $M_2(k, t)$  we obtain the expression for the dynamic structure factor, where the static structure factor  $S(k)$  and general relaxation parameters of  $i$ th orders  $\Omega_i^2$  ( $i = 1, 2, 3, 4$ ) are contained

$$\begin{aligned} S(k, \omega) = & \frac{S(k)}{2\pi} \Omega_1^2 \Omega_2^2 \Omega_3^2 (4\Omega_4^2 - \omega^2)^{1/2} \{ \Omega_1^4 \Omega_3^4 + \\ & + \omega^2 (\Omega_1^4 \Omega_4^2 - 2\Omega_1^2 \Omega_3^4 - \Omega_1^4 \Omega_3^2 + 2\Omega_1^2 \Omega_2^2 \Omega_4^2 - \\ & - \Omega_1^2 \Omega_2^2 \Omega_3^2 + \Omega_2^4 \Omega_4^2) + \omega^4 (\Omega_3^4 - 2\Omega_1^2 \Omega_4^2 + \\ & + 2\Omega_1^2 \Omega_3^2 - 2\Omega_2^2 \Omega_4^2 + \Omega_2^2 \Omega_3^2) + \omega^6 (\Omega_4^2 - \Omega_3^2) \}. \end{aligned} \quad (4)$$

Now we use the theory proposed above for the evaluation of  $S(k, \omega)$  in liquid cesium near its melting point at  $T = 308$  K. The quantities needed for the calculation are  $S(k)$  and  $\Omega_i^2$  ( $i = 1, 2, 3, 4$ ). The numerical static structure data were received by Bodensteiner et al. [5], and we use these  $S(k)$  data in our calculations.

The first two relaxation parameters  $\Omega_1^2$  and  $\Omega_2^2$  are defined as  $\Omega_1^2 = K_B T k^2 / [M S(k)]$ ,  $\Omega_2^2 = \omega_l^2 - \Omega_1^2$ , where  $\omega_l^2 = 3\Omega_1^2 S(k) + N/MV \int dr g(r) [1 - \cos(kr)] \nabla_z^2 u(r)$ . Here  $K_B T$  is thermal energy;  $g(r)$  is a radial distribution function and  $u(r)$  is a pair interparticle potential of interaction (axis  $z$  is chosen in the direction of wave vector  $k$ ). However, to calculate the second frequency parameter  $\Omega_2^2$  we use the known Hubbard-Beeby approximation [8]  $\Omega_2^2 = 3\Omega_1^2 S(k) + \omega_E^2 [1 - 3 \sin(x)/x - 6 \cos(x)/x^2 + 6 \sin(x)/x^3] - \Omega_1^2$ . Here  $x = kR_0$  with  $R_0 = 4.8 \text{ \AA}$  and Einstein frequency  $\omega_E^2$  is taken to be  $4.12 \text{ ps}^{-1}$  which is the value obtained by Bodensteiner [5]. The theoretical formulas of  $\Omega_3^2$  and  $\Omega_4^2$  cannot be used in calculations for one reason. The final result of these calculations has gross errors. Therefore these parameters can be defined by comparing theoretical and experimental results. Namely, the third and the fourth relaxation frequency parameters ( $\Omega_3^2$  and  $\Omega_4^2$ ) were found by us from two mutually independent conditions: the behavior of  $S(k, \omega)$  in the points of a central ( $\omega = 0$ ) and a side ( $\omega \neq 0$ ) maximums.

We have calculated  $S(k, \omega)$  at low- $k$  region  $k = 0.4 \sim 0.9 \text{ \AA}^{-1}$ , where high-frequency peaks were experimentally observed. The results for the representative wave vectors are shown in Fig.1. It is clear from Fig.1 that our theory describes adequately collective density exci-

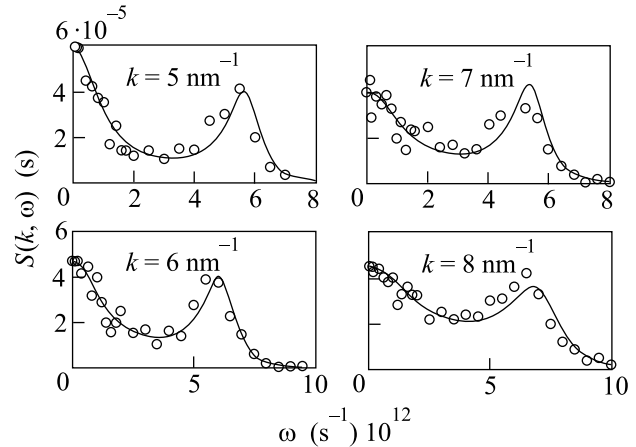


Fig.1. Theoretical (solid line) and experimental ( $\circ$ ) values of dynamic structure factor for liquid cesium near the melting point

tations in spectra of  $S(k, \omega)$  for liquid cesium. For investigated wave vector region we have achieved a good agreement with the experiment [5]. In Fig.2 we report a set of normalized dynamic structure factor  $S(k, \omega)/S(k)$  as calculated from our theory for wave vector region  $0.4 \leq k \leq 1.8 \text{ \AA}^{-1}$ . From this figure one can see certain changes of the position and altitude of the central

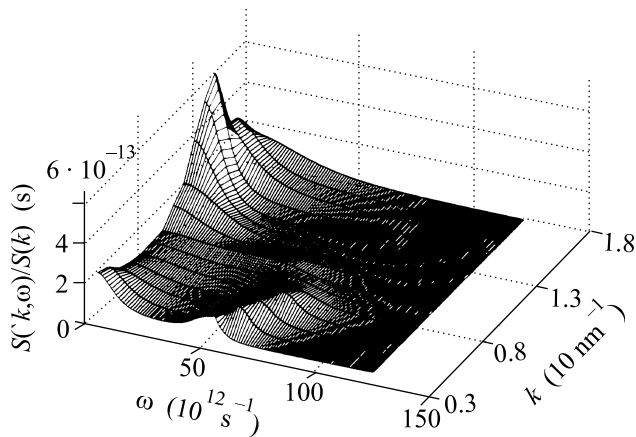


Fig.2. Dynamic structure factor calculated on the basis theory for liquid cesium at 308K

and side peaks at different values of the wave vector  $k$ . As can be seen in Fig.2, a side peaks persist up to  $k \sim 1.1 \text{ \AA}^{-1}$ , i.e., very close to the position of the first peak in the static structure factor ( $k \sim 1.4 \text{ \AA}^{-1}$ ). This again shows that the liquid supports collective excitations for wavelengths comparable with the mean interparticle spacing, a distinctive characteristic of liquid metals [6].

To understand the nature of the collective excitations below  $k = 1 \text{ \AA}^{-1}$  we have studied the behavior of the frequency-dependent non-Markovity parameter  $\varepsilon_1(k, \omega)$ . This parameter was at first entered [9] on the basis of parameter  $\varepsilon_0 = \tau_0/\tau_1$ , where the relaxation times  $\tau_0$  and  $\tau_1$  are calculated by Eq.3. By this non-Markovity parameter [10] all relaxation processes can be divided into Markovian scenario, when  $\varepsilon_0 \rightarrow \infty$ , quasi-Markovian scenario at  $\varepsilon_0 > 1$  and non-Markovian scenario at  $\varepsilon_0 \sim 1$ . The generalized parameter  $\varepsilon_1(k, \omega)$  is defined at fixed  $k$  by the expression

$$\varepsilon_j(\omega) = \left[ \frac{\mu_{j-1}(\omega)}{\mu_j(\omega)} \right]^{1/2}, \quad \mu_j(\omega) = \left\{ \text{Re} \left[ \int dt M_j e^{i\omega t} \right] \right\}^2. \quad (5)$$

Here  $\mu_j(\omega)$  is the power spectra of the  $i$ -th relaxation level was introduced. In Fig.3 we present the results of calculations for the frequency-dependent non-Markovity parameter  $\varepsilon_1(k, \omega)$  at several values of wave vectors  $k$ . It can be seen from Fig. 3 that the values of  $\varepsilon_1(k, \omega)$  show the alternation of maxima and minima. In addition,  $\varepsilon_1(k, \omega)$  and  $S(k, \omega)$  maxima in the low- $k$  region are located on approximately the same frequencies, which are associated with collective excitations in liquid metal. The amplitudes of these peaks quickly fall down with  $k$  increasing. This is due to the amplification of non-Markovity effects. The occurrence of  $\varepsilon_1(k, \omega)$

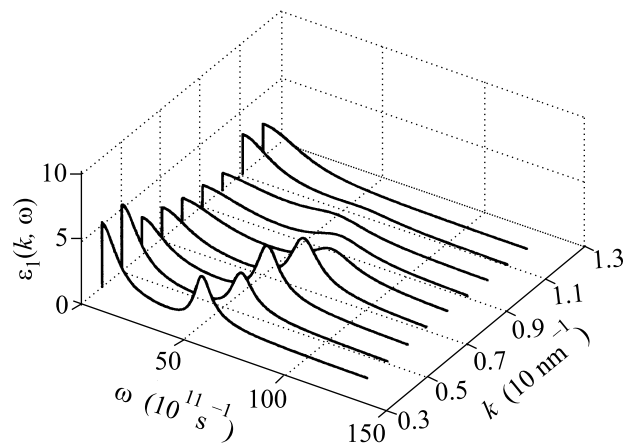


Fig.3. Frequency dependence of non-Markovity parameter  $\varepsilon_1(k, \omega)$  for  $4 < k < 12 \text{ nm}^{-1}$

peaks in the region of collective excitations indicates the essential amplification of quasi-Markovity at propagating of ion density fluctuations. High-frequency collective excitations disappear smoothly with  $k$  increasing, simultaneously non-Markovity is further enhanced. Similarly,  $\varepsilon_1(k, \omega = 0)$  increasing means enhancement of randomness in thermal motion of particles. Thus, the observed frequency behavior of the parameter  $\varepsilon_1(k, \omega)$  consists in consecutive alternation of quasi-Markov and non-Markov relaxation scenarios of behavior. The similar alternation cannot be received within the framework of any other theory.

In this Letter, we have presented the theory, based on Zwanzig-Mori's MF formalism [7] and the idea of TSI, which allows to describe the dynamic structure spectra in all experimentally investigated region of the wave vector. The long-range memory and the short time correlations have affected the analysis of non-Markov properties of the collective dynamics in liquid cesium. In this way we are going to establish the non-Markov nature of collective excitations in liquid cesium at the low- $k$  values.

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