

Dynamic Structure Factor in Liquid Cesium on the Basis of Time-Scale Invariance of Relaxation Processes[¶]

R. M. Yulmetyev*, A. V. Mokshin*, P. Hänggi**, and V. Yu. Shurygin***

* Kazan State Pedagogical University, 420021 Kazan, Russia

e-mail: rmy@ntp.ksu.ras.ru; mav@ntp.ksu.ras.ru

** University of Augsburg, D-86135 Augsburg, Germany

*** Yelabuga State Pedagogical Institute, 423630 Yelabuga, Russia

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 a careful analysis of the dynamic structure factor $S(k, \omega)$ spectra. High-frequency peaks are appreciable in $S(k, \omega)$ for 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 damping of these excitations is still a challenge in liquid metals, where the dynamics is conditioned by interacting electron gas effects. So, a recent INS experiment on liquid cesium near its melting point was carried out by Bodensteiner *et al.* in Grenoble [5]. The results of their experiment have shown that high-frequency collective excitations exist in this system for wave vector region $k < 1.1 \text{ \AA}^{-1}$. MD simulation performed by Kambayashi and Kahl [2] validated fully the findings of INS in liquid cesium. The analysis of collective excitations that extend 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 fluctuations are given by

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

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

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

Here, we introduce the first general relaxation frequency parameter Ω_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 pro-

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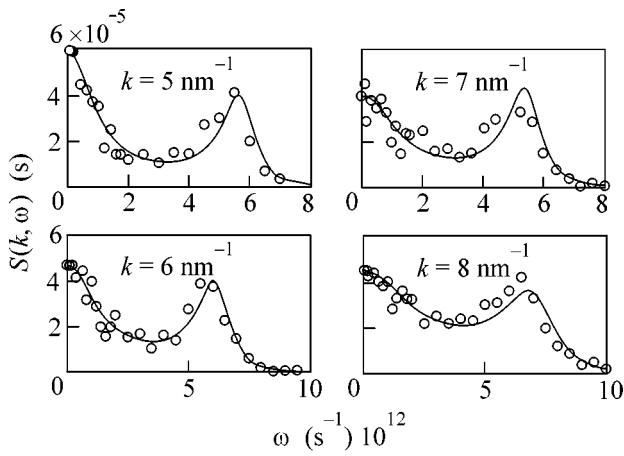


Fig. 1. Theoretical (solid line) and experimental (○) values of the dynamic structure factor for liquid cesium near the melting point.

cess (for example, to a density fluctuations in liquids), which can be easily taken into account by MF formalism.

According to the definition, for ergodic processes the correlation functions $M_0(k, t) = F(k, t)$, $M_1(k, t)$, ..., $M_i(k, t)$ 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 by the equation

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

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

These time scales T_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 an approach allows one to receive an 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 system investigated. In the case of simple liquid metals, by analogy with the hydrodynamics region, we propose that only three variables, namely local density, local momentum density, and local energy density, are 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 clo-

sure: $M_4(k, t) \approx M_3(k, t)$. By means of the Laplace transformation of the corresponding equations for $M_0(k, t) = F(k, t)$, $M_1(k, t)$, $M_2(k, t)$, we obtain an expression for the dynamic structure factor in which the static structure factor $S(k)$ and general relaxation parameters of the i th orders ω_i^2 ($i = 1, 2, 3, 4$) are contained:

$$\begin{aligned} S(k, \omega) = & \frac{S(k)}{2\pi} \left\{ \omega_1^2 \omega_2^2 \omega_3^2 \left(4\omega_4^3 - \omega^2 \right)^{1/2} \left(\omega_1^4 \omega_3^4 \right. \right. \\ & + \omega^2 \left(\omega_1^4 \omega_4^2 - 2\omega_1^2 \omega_3^4 - \omega_1^4 \omega_3^2 \right) + 2\omega_1^2 \omega_2^2 \omega_4^2 \\ & - \omega_1^2 \omega_2^2 \omega_3^2 + \omega_4^2 \omega_2^2 \left. \right) + \omega^4 \left(\omega_3^4 - 2\omega_1^2 \omega_4^2 \right. \\ & \left. + 2\omega_1^2 \omega_3^2 - 2\omega_2^2 \omega_4^2 + \omega_2^2 \omega_3^2 \right) + \omega^6 \left(\omega_4^2 - \omega_3^2 \right) \}. \end{aligned} \quad (4)$$

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 ω_i^2 ($i = 1, 2, 3, 4$). The numerical static structure data were obtained by Bodensteiner *et al.* [5], and we use these $S(k)$ data in our calculations. The first two relaxation parameters ω_1^2 and ω_2^2 are defined as $\omega_1^2 = K_B T k^2 / [M S(k)]$, $\omega_2^2 = \omega_E^2 - \omega_1^2$, where $\omega_E^2 = 3\omega_1^2 S(k) + N/MV \int dr g(r) [1 - \cos(kr)]^2 u(r)$. Here, $K_B T$ is the thermal energy, $g(r)$ is the radial distribution function, and $u(r)$ is the pair interparticle interaction potential (the z axis is chosen in the direction of the wave vector k). However, to calculate the second frequency parameter ω_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 $R_0 = 4.8$ Å and the Einstein frequency ω_E^2 is taken to be 4.12 ps $^{-1}$, which is the value obtained by Bodensteiner [5]. The theoretical formulas for ω_3^2 and ω_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, we found the third and the fourth relaxation frequency parameters (ω_3^2 and ω_4^2) were found by us from two mutually independent conditions: the behavior of $S(k, \omega)$ in the points of central ($\omega = 0$) and side ($\omega \neq 0$) maximums.

We have calculated $S(k, \omega)$ in the low- k region $k = 0.4 \sim 0.9$ Å $^{-1}$, where high-frequency peaks were experimentally observed. The results for the representative wave vectors are shown in Fig. 1. It is clear in Fig. 1 that our theory describes adequately the collective density excitations in spectra of $S(k, \omega)$ for liquid cesium. For the investigated wave-vector region, we have achieved a good agreement with the experiment [5]. In Fig. 2, we

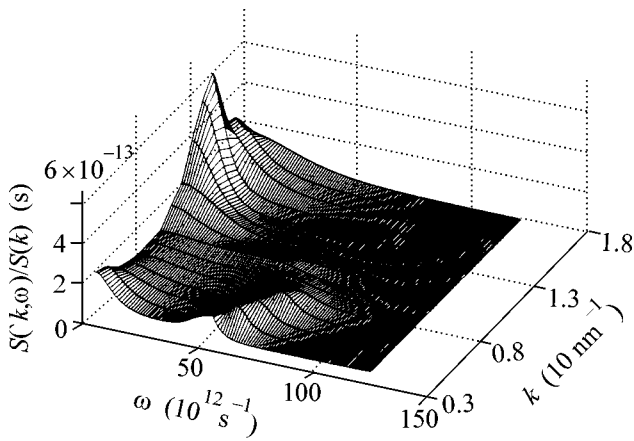


Fig. 2. Dynamic structure factor calculated on the basis theory for liquid cesium at 308 K.

report a set of normalized dynamic structure factors, $S(k, \omega)/S(k)$, as calculated from our theory for the wave vector region $0.4 \leq k \leq 1.8 \text{ \AA}^{-1}$. In this figure, one can see certain changes in the position and altitude of the central and side peaks at different values of the wave vector \mathbf{k} . As can be seen in Fig. 2, 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 τ_0 and τ_1 are calculated by Eq. (3). By this non-Markovity parameter [10], all relaxation processes can be divided into a Markovian scenario, when $\varepsilon_0 \rightarrow \infty$, a quasi-Markovian scenario at $\varepsilon_0 > 1$, and a non-Markovian scenario at $\varepsilon_0 \sim 1$. The generalized parameter $\varepsilon_1(k, \omega)$ is defined at fixed k by the expression

$$\varepsilon_j(\omega) = \left[\frac{\mu_{j-1}(\omega)}{\mu_j(\omega)} \right]^{1/2}, \quad (5)$$

$$\mu_j(\omega) = \left\{ \text{Re} \int dt M_j e^{i\omega t} \right\}^2.$$

Here, $\mu_j(\omega)$ is the power spectra of the i th relaxation level that 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 in Fig. 3 that the values of $\varepsilon_1(k, \omega)$ show an 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 frequen-

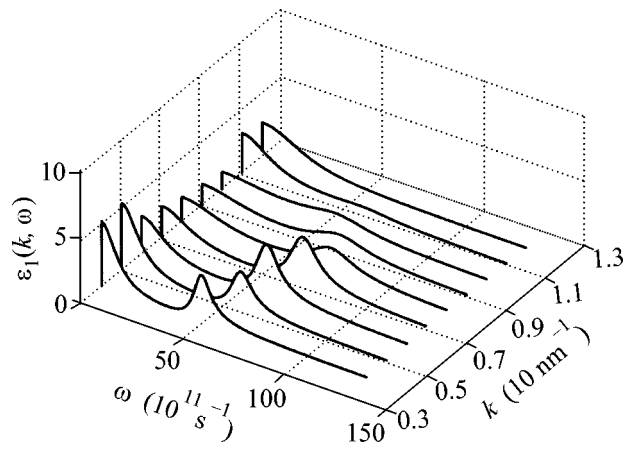


Fig. 3. Frequency dependence of non-Markovity parameter $\varepsilon_1(k, \omega)$ for $4 < k < 12 \text{ nm}^{-1}$.

cies that are associated with collective excitations in liquid metal. The amplitudes of these peaks quickly fall as k increases. This is due to the amplification of non-Markovity effects. The occurrence of $\varepsilon_1(k, \omega)$ peaks in the region of collective excitations indicates an essential amplification of quasi-Markovity on propagation of ion density fluctuations. High-frequency collective excitations disappear smoothly with increasing k , and simultaneously non-Markovity is further enhanced. Similarly, an increase in $\varepsilon_1(k, \omega = 0)$ means an enhancement of randomness in the thermal motion of particles. Thus, the frequency behavior of the parameter $\varepsilon_1(k, \omega)$ observed consists in a consecutive alternation of quasi-Markovian and non-Markovian relaxation scenarios of behavior. Such an 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 one to describe the dynamic structure spectra in all experimentally investigated regions of the wave vector. The long-range memory and the short time correlations have affected the analysis of non-Markovian properties of the collective dynamics in liquid cesium. In this way, we are going to establish the non-Markovian nature of collective excitations in liquid cesium at low k values.

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