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Time-scale invariance of relaxation processes of density fluctuation in slow neutron scattering in liquid cesium

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The realization of the idea of time-scale invariance for relaxation processes in liquids has been performed by the memory functions formalism. The best agreement with experimental data for the dynamic structure factor $S(k,\omega)$ of liquid cesium near melting point in the range of wave vectors ($0.4\ \text{Å}^{-1} \leqslant k \leqslant 2.55\ \text{Å}^{-1}$) is found with the assumption of concurrence of relaxation scales for memory functions of third and fourth orders. Spatial dispersion of the first four points in the spectrum of the statistical parameter of non-Markovity $\epsilon_i(k,\omega)$ at $i=1,2,3,4$ has allowed us to reveal the non-Markov nature of collective excitations in liquid cesium, connected with long-range memory effect.

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The dynamic structure factor $S(k,\omega)$ of liquid metals (lithium, sodium, rubidium, lead, cesium, aluminum, potassium) represents unique information on the collective excitations in these systems (see Ref. [1]). Most of existing theories for $S(k,\omega)$ are based on models of the linearized and generalized hydrodynamics [2]. Despite much effort and considerable recent progress, understanding of experimental data for liquid metals remains an interesting challenge. Here adequate understanding and explanation of high-frequency collective excitations does not exist. The reason is that the nature of such excitations in liquid metals is not described by any of hydrodynamic models. On account of specific short-range and oscillatory behavior of ion-ion potential in liquid metals, the hydrodynamics here is not applicable.

In the present work, for an explanation of a specific nature of high-frequency collective excitations in liquid cesium [3] we use one of most fundamental ideas of modern physics—the idea of invariance. In particular, we suggest the idea of time-scale invariance of relaxation processes in liquids. Experimental data on $S(k,\omega)$ give direct information about relaxation processes of density fluctuation in liquids. Under the assumption, for any experimentally observable relaxation process, there corresponds a multilevel hierarchy of interconnected relaxation processes. Actually, in experiment the ''top'' of its relaxation ''iceberg'' is observed only. On a certain relaxation level, an invariance (equiscaling) of two nearest interconnected relaxation processes can exist. Such invariance can be easily taken into account by the memory functions formalism, which most adequately describes nonequilibrium statistical processes in condensed matter physics.

Later we consider a normalized time correlation function (TCF) $a(t)=\langle \delta A^*(0)\delta A(t)\rangle / \langle |\delta A(0)|^2\rangle$ of particle-density fluctuation in liquid metal $\delta A(t)=A(t)-\langle A(t)\rangle$, where $\delta A(t)=N^{-1/2}\sum_{j=1}^{N}\exp(ikr_j)$, k is wave vector, and r_j defines the position of the jth particle of the liquid. With the help of Zwanzig and Mori's projection operators method [4,5] it is possible to construct the infinite chain of connected non-Markov kinetic equations as follows:

$$\frac{dM_i(t)}{dt} = -\Omega_{i+1}^2 \int_0^t d\tau M_{i+1}(t-\tau) M_i(\tau), \quad i=0,1,\ldots, \tag{1}$$

where $M_0(t)=a(t)$. Here $M_i(t)$ is a memory function of ith order and Ω_i^2 are general relaxation parameters with the dimension of the square of frequency. These parameters are connected with even frequency moments of spectral density of TCF $a(t)$ by the following relationship [6] $\Omega_1^2=I_2$, $\Omega_2^2=I_4I_2^{-1}-I_2$, $\Omega_3^2=(I_6I_2-I_4^2)/(I_4I_2-I_2^3)$.

Every relaxation process can be described with the help of a characteristic time scale usually named as relaxation time. So, for example, the relaxation time for initial TCF $a(t)$ can be determined as follows $\tau_a=\mathrm{Re}\int_0^\infty dt a(t)$. Similarly, relaxation time on the second relaxation level [at $i=1$ in Eqs. (1)] for memory function $M_1(t)$ would be expressible as $\tau_1=\mathrm{Re}\int_0^\infty dt M_1(t)$, where the symbol Re means the real part. It is convenient to describe long-range memory effects in the underlying system with the help of time scales τ_a and τ_{M_1}. For example, the presentation of the dimensionless non-Markovity parameter was introduced earlier in Ref. [6], $\epsilon_1=\tau_0/\tau_1$, as an criterion of describing of non-Markovity for any relaxation processes. As pointed out in Ref. [6] values of ϵ_1 allow to obtain a quantitative and qualitative estimate of non-Markovity effects and statistical memory in relaxation processes. Parameter ϵ_1 allows to divide all relaxation processes into three important cases. Markovian processes correspond to $\epsilon_1\to\infty$, while quasi-Markovian processes are appropriate in situations with $\epsilon_1 \gg 1$ and $\epsilon_1 > 1$. The limiting case $\epsilon_1 \sim 1$ describes non-Markovian processes. In this case the time scale of memory processes and correlations (or junior and senior memory functions) coincide with each other. Thus, the introduced parameter ϵ_1 characterizes non-Markovity and memory effects for any relaxation processes.

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The infinite set of values of parameters ϵ_i, where $i=1,2,3,\ldots$, was also entered on the basis of the simple formula $\epsilon_i = \tau_{i-1}/\tau_i$, where τ_i is a relaxation time of the memory function of ith order [7]. The whole set of values of non-Markovity parameter ϵ_i forms the statistical spectrum, which is connected with collective and statistical properties of the system and allows also to estimate in detail the non-Markovian properties of the underlying relaxation process. In Ref. [8] the conception of non-Markovity parameter for the frequency-dependent case was generalized . This parameter is determined by the following expression $\epsilon_i(\omega) = \{\mu_{i-1}(\omega)/\mu_i(\omega)\}^{1/2}$ at the fixed wave vector k. Here $i=1,2,3\ldots$ and $\mu_i(\omega)$ is the power frequency spectrum of the ith relaxation level, which is defined in the following way $\mu_j(\omega) = [\mathrm{Re}\int_0^\infty dt e^{i\omega t} M_j(t)^2$.

The appropriate values of $\epsilon_i(\omega)$ and ϵ_i will correspond to every jth equation of the chain (1). As the chain of the Eq. (1) is infinite, the sets of ϵ_i and $\epsilon_i(\omega)$ are also infinite. Now let us use the approximation $M_{i+1}(t) \approx M_i(t)$. It means the approximate equality of relaxation time scales of memory functions of ith and $(i+1)$th orders, i.e., $\tau_{i+1} \approx \tau_i$. Then the non-Markovity parameter for the whole frequency range is approximately equal to unity, $\epsilon_{i+1}(\omega) \sim 1$ (and also $\epsilon_{i+1} \sim 1$), and chain (1) becomes closed. Applying Laplace transform to the ith equation of the chain (1) we get $\tilde{M}_i(s) = [-s + (s^2 + 4\Omega_{i+1}^2)^{1/2}]/2\Omega_{i+1}^2$.

The results of experiment for liquid cesium were published in Ref. [3]. The dynamic structure factor $S(k,\omega)$ has been measured by inelastic slow neutron scattering (INS) near the melting point at $T=380$ K. The wave vector k changes in the range from 0.2 Å^{-1} up to 2.55 Å^{-1}. The numerical results for $S(k)$ were obtained from experimental data [3] too.

It is well known that $S(k,\omega)$ is connected with TCF of density fluctuation in the following way: $S(k,\omega) = [S(k)/\pi] \lim_{\epsilon \to +0} \mathrm{Re}[\tilde{a}(k, i\omega + \epsilon)]$, where Laplace transform $\tilde{a}(k,s) = \int_0^\infty dt e^{-st} a(k,t)$ was found by us as follows. We have taken advantage of the correlation approximation for the fourth order memory function [9]

$$M_4(t) \approx M_3(t). \tag{2}$$

From the physical point of view it means the concurrence of time scales of TCF's $M_3(t)$ and $M_4(t)$. In this case the chain of the connected kinetic equations (1) becomes a system consisting of four equations. Using Laplace transform, we receive the following equation for the dynamic structure factor $S(k,\omega)$:

$$\begin{aligned} S(k,\omega) = \frac{S(k)}{2\pi} & \Omega_1^2\Omega_2^2\Omega_3^2(4\Omega_4^2 - \omega^2)^{1/2}\{\Omega_1^4\Omega_3^4 + \omega^2 \\ & \times(-2\Omega_1^2\Omega_3^4 + \Omega_1^4\Omega_4^2 - \Omega_1^4\Omega_3^2 + 2\Omega_1^2\Omega_2^2\Omega_4^2 \\ & - \Omega_1^2\Omega_2^2\Omega_3^2 + \Omega_2^4\Omega_4^2) + \omega^4(\Omega_3^4 - 2\Omega_1^2\Omega_4^2 + 2\Omega_1^2\Omega_3^2 \\ & - 2\Omega_2^2\Omega_4^2 + \Omega_2^2\Omega_3^2) + \omega^6(\Omega_4^2 - \Omega_3^2)\}^{-1}. \end{aligned} \tag{3}$$

Relaxation frequency parameters Ω_1^2 and Ω_2^2 are defined as follows [11]:

$$\Omega_1^2 = K_B T k^2 [m S(k)]^{-1}; \quad \omega_1^2 = \Omega_1^2; \quad \Omega_2^2 = \omega_2^2 - \omega_1^2;$$

$$\omega_2^2 = 3\omega_1^2 S(k) + \omega_l^2;$$

$$\omega_l^2 = N/mV \int drg(r)[1 - \cos(kr)]\nabla_z^2 u(r). \tag{4}$$

In Eqs. (4) the following designations are introduced: $K_B T$ is thermal energy, $g(r)$ is a radial distribution function of particles, $u(r)$ is a pair interparticle potential of interaction, and axis z is chosen in the direction of a wave vector k. Calculating the frequency parameter Ω_2^2 we use the well-known approximation [10] $\Omega_2^2 = 3\Omega_1^2 S(k) + \omega_E^2\{1 - [3\sin(kR_0)/kR_0] - [6\cos(kR_0)/(kR_0)^2] + [6\sin(kR_0)/(kR_0)^3]\} - \Omega_1^2$, where ω_E is the Einstein frequency. In our case ω_E has the following value $\omega_E = 4.12 \times 10^{12}\,\mathrm{s}^{-1}$ [3]. This frequency parameters can also be calculated through I_i $(i=2,4)$.

Theoretical formulas for calculation of relaxation frequency parameters Ω_3^2 and Ω_4^2 are also known [11]. However the final result of these calculations contains some errors. For example, in paper [11] it is shown that results of calculated frequency moments in papers [12–14], vary from 10% to 50%, and the distinction reaches up to 30 times for separate values of the wave vector. Therefore it is more convenient to obtain these parameters by comparing results of theory and experiment. Relaxation frequency parameter Ω_4^2 is easy to find from comparison of developed theory with experiment on zero frequency. Namely, it follows $\Omega_4^2 = \pi^2\Omega_1^4\Omega_3^4[S(k,0)]^2([S(k)]^2\Omega_2^4)^{-1}$ from Eq. (3) at $\omega \to 0$.

The spectrum of $S(k,\omega)$, Eq. (3), allows investigations of collective excitations in liquid cesium to be made in detail. Our analysis show that the position of collective excitation peak $\omega_c(k)$ in spectrum $S(k,\omega)$ depends on the combination of frequencies Ω_1^2, Ω_2^2, Ω_3^2, and Ω_4^2. Our numerical calculations demonstrate that $\omega_c(k)$ value is most sensitive to relaxation frequency Ω_2^2. On the other hand, collective effects turn out to be connected with non-Markov processes in liquids.

In Fig. 1 the comparison of our theory (solid line) and experimental data (circles) [3] for $S(k,\omega)$ for liquid cesium at $T=380$ K is shown. From Fig. 1 it is evident that our theory absolutely agrees with the experiment in the whole range of values of wave vector k. It is possible to see the good qualitative coincidence between the experiment and our theory from Fig. 2. Here dispersion of the frequency of collective excitations $\omega_c(k)$, obtained from the position of lateral peaks (the points present experimental data; the circles are our theoretical values), is presented. We calculated the first four points in a statistical spectrum of the frequency-dependent non-Markovity parameter $\epsilon_i(k,\omega)$ for the whole range of values of the wave vector k. The results of such calculations are shown in Fig. 3. In our opinion, the parameter $\epsilon_1(k,\omega)$ represents special interest. From Fig. 3 it is apparent that this parameter has maxima on frequencies that coincide with collective excitations in $S(k,\omega)$. The spectrum

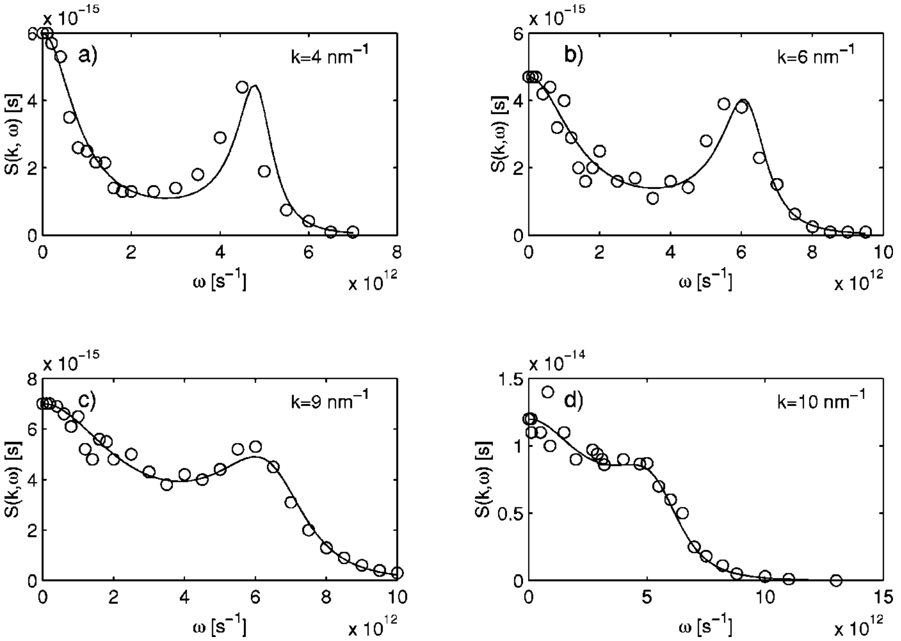

FIG. 1. Theoretical (solid line) and experimental [3] (○ ○ ○ ○) values of dynamical structure factor $S(k,\omega)$ for liquid cesium at $T=380$ K at various wave vectors $k=|\mathbf{k}|$.

of $S(k,\omega)$ falls down smoothly at large values of k, and the frequency-dependent non-Markovity parameter also falls down smoothly to zero. Moreover, a ‘‘burst’’ of values $\epsilon_1(k,\omega)$ is observed on common frequencies with $S(k,\omega)$. As indicated by Fig. 3, the non-Markovity parameter $\epsilon_i(\omega)$ for this range of frequencies ω must satisfy the condition $\epsilon_i(k,\omega)>1$. The non-Markovity parameter $\epsilon_1(k,\omega)$ has the distinct expressed maximum on frequencies, relevant to collective excitations. Proceeding from the received results, it is reasonable to speak about the non-Markov nature of collective excitations in liquid cesium. This important conclusion must be taken into account while constructing the appropriate theories. The behavior of $\epsilon_i(k,\omega)$ for levels $i=2,3,4$ is very interesting here. Further calculation shows that the relationship $\epsilon_3(k,\omega)\approx 1$ takes place for the high k-value range 1.15 Å$^{-1}\leqslant k\leqslant 2.55$ Å^{-1} and for all frequencies ω. Because of this, the more simple approximation $M_3(t)\approx M_2(t)$ can be applied for this case. Moreover, there are cases in which $\epsilon_2(k,\omega)\approx 1$ for all ω. It is possible to assume that good agreement with the experiment gives correlation approximation for the memory function of the second order $M_2(t)\approx M_1(t)$ in these cases.

Thus, the frequency-dependent non-Markovity parameter $\epsilon_i(k,\omega)$ introduced in Ref. [8] allows us to reveal two important features. First, its behavior allows us to judge the properties of non-Markovity in the whole range of the frequency spectrum and at various values of the wave vector k. Then, with its help it is possible to judge the applicability of correlation approximation of the junior order, for which less difficult calculations are required.

The results of this Brief Report can be summarized as follows.

(i) $S(k,\omega)$ for liquid cesium is found on the basis of the hypothesis of time-scale invariance of relaxation processes in liquids. We have assumed that relaxation times of memory functions $M_4(t)$ and $M_3(t)$ are approximately equal in this case and relaxation time scales are invariant. Therefore, we have used correlation approximation for the memory function of fourth order, $M_4(t)$, for closing the chain of the connected kinetic equations (1). As a result we have received good agreement with the experiment for all values of wave vector k (0.4 Å$^{-1}\leqslant k\leqslant 2.55$ Å^{-1}).

(ii) For the estimation of the received results the frequency-dependent parameter of non-Markovity $\epsilon_i(\omega)$ ($i=1$, 2, 3, and 4) was calculated for all the values of the wave vector k. It turned out that the first point in the spectrum of non-Markovity parameter $\epsilon_1(\omega)$ has frequency dependence similar to the behavior of the dynamic structure factor for liquid cesium. The maximum of $\epsilon_1(k,\omega)$ and $S(k,\omega)$ for values of the wave vector 0.4 Å$^{-1}\leqslant k\leqslant 2.55$ Å^{-1} appear at the same frequencies.

(iii) On the basis of our calculations we have established

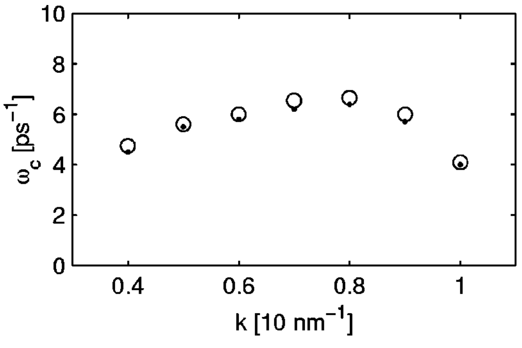

FIG. 2. Comparison of the values of frequency of collective excitations in liquid cesium $\omega_c=\omega_c(k)$ at $T=380$ K with calculated values from experimental data [3] (· · · ·) and our theory (○ ○ ○ ○).

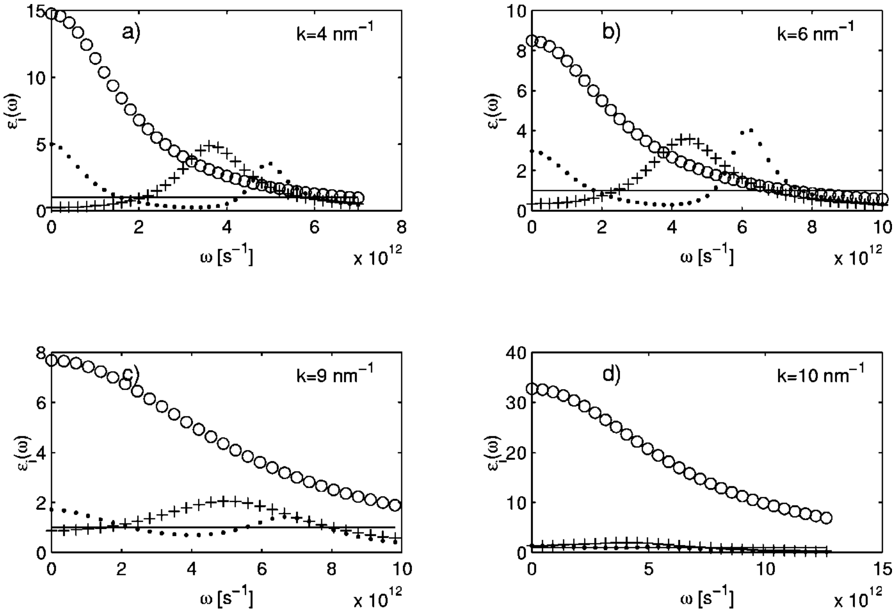

FIG. 3. Frequency dependence of the first four points in statistical spectrum of non-Markovity parameter $\epsilon_i=\epsilon_i(\omega)$; $(\cdot\ \ \cdot\ \ \cdot\ \ \cdot)$ correspond to $i=1$, $(+\ \ +\ \ +\ \ +)$ relate to $i=2$, (○ ○ ○ ○) present $i=3$, solid line reflects values at $i=4$. In a wave vector range $0.4\ \text{Å}^{-1} \leqslant k \leqslant 1.1\ \text{Å}^{-1}$ collective excitations exist.

the non-Markov nature of collective excitations at the microscopic level in liquid cesium. It should be pointed out that the developed approach is true, especially for the solution of nonperturbative problems. Nevertheless, we believe that a systematic and general theoretic approach, such as we have expounded, should play a useful role in analyzing and classifying experimental data simulations and more elaborate models. It is especially true for the construction of theories describing high-frequency and short-range relaxation processes. The calculated frequency parameter $\epsilon_1(\omega)$ for every concrete value of wave vector k allows to describe the effects of amplification or attenuation of non-Markovity within the whole frequency interval. From the preceding it is clear that the idea of time-scale invariance has large prospects for the description of high- and short-wave stochastic and relaxation processes in liquids.

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[9] The introduction of approximation (2) is related to a specific feature of liquid metals. In particular, it is connected with the short range of ion-ion potential. It can be shown that time correlation of Fourier components of a local momentum density, local energy density, and local current density occur in memory functions $M_1(t)$, $M_2(t)$, and $M_3(t)$, respectively. Space and momentum functions arise in appropriate dynamic variables, depending on position and momentum of molecules of liquids. The reapproachment of time-relaxation scale on the third and fourth relaxation levels occurs through the entanglement of these functions and the short range of ion-ion interactions.

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