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The study of high-frequency dynamics in liquid magnesium by memory-function formalism and computer simulation molecular dynamics

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Abstract. The study of structure and dynamics of particles in liquid magnesium at the two thermodynamical states (at the temperature $T = 953$ K and $T = 1063$ K) has been performed by computer simulation molecular dynamics with the 'glue' interparticle potential. The calculated equilibrium terms are compared with the experimental data on X-ray scattering. The results of comparative analysis to show adequacy of choice of the interparticle potential for liquid magnesium. The study of collective properties of the magnesium particles on the basis of the dynamic structure factor, $S(k, \omega)$, for eight wave-numbers $k = 0.5$, 0.7, 0.9, 1.1, 1.4, 1.6, 1.8 и 2.0 Å^{-1} are carry out. The theoretical analysis of $S(k, \omega)$ by Zwanzig-Mori's memory-function formalism on the basis of N.N. Bogoliubov's ideas about reduced description of statistical systems and the hierarchy of relaxation time-scales are executed. The results of theoretical calculations are in a good agreement with computer simulation molecular dynamics data.

Keywords: molecular dynamics, microscopical dynamics, collective excitations, dynamic structure factor.

1. Introduction

The fundamental investigations of physical mechanisms of collective excitations in liquids are one of the most interesting tasks in the physics of condensed matter [1, 2]. It is well-known, that collective properties of liquid metals outside the strict hydrodynamic region are characterized some specific features. For example, the dynamic structure factor, $S(k, \omega)$, has three-peak structure, so called, Rayleigh-Mandelshtam-Brillouin triplet (RMB). The similar triplet was detected in many other liquids by INS experiments [3, 4, 5] and inelastic coherent X-ray scattering [6, 7, 8, 9]. Furthermore, nonlinear increasing the speed of sound with wave-number, k, changes (so called 'positive dispersion' of the sound velocity), and another effects are observed. The registration of these features is cause of rapid development the experimental research as well as theoretical one (see review [10]). At the present time, there are several theoretical approaches to description RMB-like triplet of the dynamic structure factor, $S(k, \omega)$, in microscopic dynamics region. Approach, which developed in the framework of Zwanzig-Mori's memory-function formalism [11, 12, 21, 14] on base of *self-consistent* presentation of third order memory function,

by way of second order memory function [15]; approach based on the *semi-empirical* modified hydrodynamical model [16]. Recently, the authors of [17] developed new approach for description RMB-like triplet and 'positive dispersion' of the sound velocity on base of the mechanism of 'two-canal' relaxation. First 'canal' corresponded, so-called, thermal relaxation; second − is connecting with viscous relaxation (see Ref. [17] for more the detail). In this work molecular dynamics computer simulation with the purpose the testing interparticle potential [18] for the description of microscopic structure and dynamics of particles in liquid magnesium was carried out, and we develop new theoretical approach on base of the fundamental N.N. Bogoliubov's ideas about reduced description of statistical systems and hierarchy of the relaxation time scales.

2. Details of computer simulation molecular dynamics

Computer simulation molecular dynamics of liquid magnesium at the two thermodynamical states was carried out: near the melting point with the temperature $T = 953$ K ($T_m = 923$ K) and numerical density $n = 0.0383$ Å^{-3} (mass density $\rho_\mu = 1.545$ g/cm^3) and at the temperature $T = 1063$ K ($n = 0.0355$ Å^{-3}, $\rho_\mu = 1.433$ g/cm^3). The studied system of $N = 4000$ particles in a cubic cell with periodic boundary conditions. Particles interact through the so-called 'glue' potential [18]:

$$E_{pot} = E_{pair} + E_{glue} = \sum_{i<j} \psi(r_{ij}) + \sum_i U(\overline{\rho}_i), \tag{1}$$

$$\overline{\rho}_i = \sum_j \rho_{ij}. \tag{2}$$

Where $\psi(r)$ − is the short-range pair potential, $\rho(r)$ − is the function of atomic density, $U(\overline{\rho})$ − is the multi-particle 'glue' function. The functions of $\psi(r)$, $\rho(r)$ and $U(\overline{\rho})$ are shown in Fig. 1.

To reduce the time of calculations, we neglected particle interaction at a distance $r \geq r_c$, where $r_c = 6.679$ Å − is the cutting radius of the potential. For the numerical integration the equation of motion we used the *velocity Verlet algorithm* [19] with time step 10^{-14} sec. 10000 time steps were executed to bring the system to an equilibrium state, and 50000 time steps were executed to average the time correlation functions. The averaging procedure were executed over the number of particle and time.

3. Theoretical framework

Let us consider the normalized time correlation function (NCF)

$$\phi_k(t) = \frac{\langle \delta \rho_k(t) \delta \rho_{-k}(0) \rangle}{S(k)} \tag{3}$$

of density fluctuations $\delta \rho_k(t) = 1/N \sum_{j=1}^N \exp(i\mathbf{k}\mathbf{r}_j(t))$ in a liquid. Where $S(k) = \langle |\delta \rho_k(0)|^2 \rangle$ − is the static structure factor, $\mathbf{k}$ − is the wave-vector, and $\mathbf{r}_j(t)$ − is the radius-vector of j-particle position at the moment of time t. The function $\phi_k(t)$ to satisfied the conditions of normalization and attenuation of correlations:

$$\lim_{t \to 0} \phi_k(t) = 1, \qquad \lim_{t \to \infty} \phi_k(t) = 0. \tag{4}$$

In the framework of Zwanzig-Mori's memory function formalism [11, 12, 21, 14] we can to describe the time evolution of the TCF $\phi_k(t)$ with follow kinetic equation:

$$\frac{d}{dt} M_k^{(i)}(t) = -\Delta_k^{(i+1)} \int_0^t M_k^{(i+1)}(t-\tau) M_k^{(i)}(\tau) d\tau, \qquad i = 0, 1, 2, \dots . \tag{5}$$
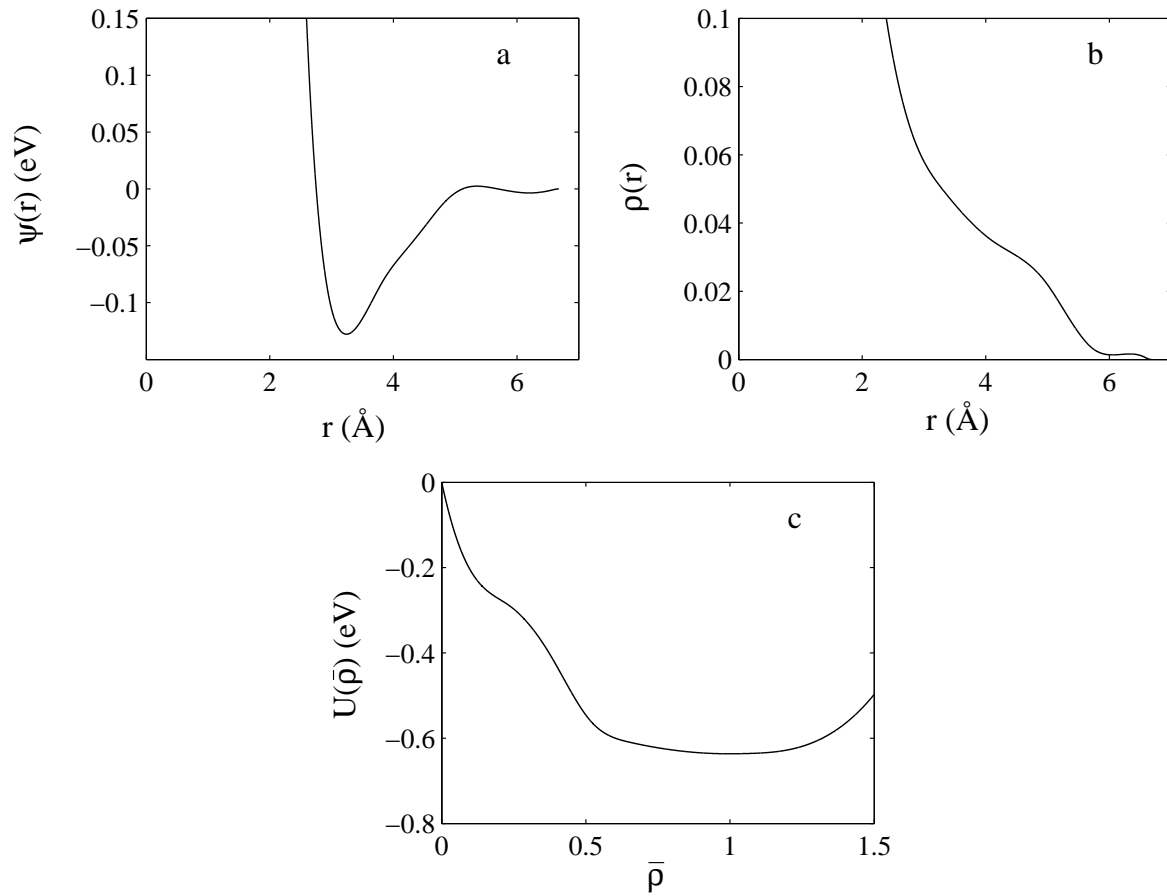
Figure 1. Interparticle potential of liquid magnesium [18].

Where $\Delta_k^{(i)}$ – is the frequency relaxation parameter with the dimension of the square of frequency, $M_k^{(i)}(t)$ – is the ith order of memory function (MF). In particular, with $i = 0$ we have $M_k^{(0)}(t) = \phi_k(t)$. By solving the Eq. (5) with help Laplace-transformation

$$\widetilde{f}(s) = \int_0^\infty dt e^{-st} f(t),\tag{6}$$

we can to obtain the follow recurrent relation

$$\widetilde{M}_k^{(i)}(s) = [s + \Delta_k^{(i+1)} \widetilde{M}_k^{(i+1)}(s)]^{-1}, \qquad i = 0, 1, 2, \dots,\tag{7}$$

where introduced the relaxation parameters $\Delta_k^{(i)}, \quad i = 1, 2, 3, \dots,$

$$\Delta_k^{(1)} = \omega_k^{(2)},$$

$$\Delta_k^{(2)} = \frac{\omega_k^{(4)}}{\omega_k^{(2)}} - \omega_k^{(2)},$$

$$\Delta_k^{(3)} = \frac{\omega_k^{(6)} \omega_k^{(2)} - \omega_k^{(4)2}}{\omega_k^{(4)} \omega_k^{(2)} - \omega_k^{(2)3}},\tag{8}$$
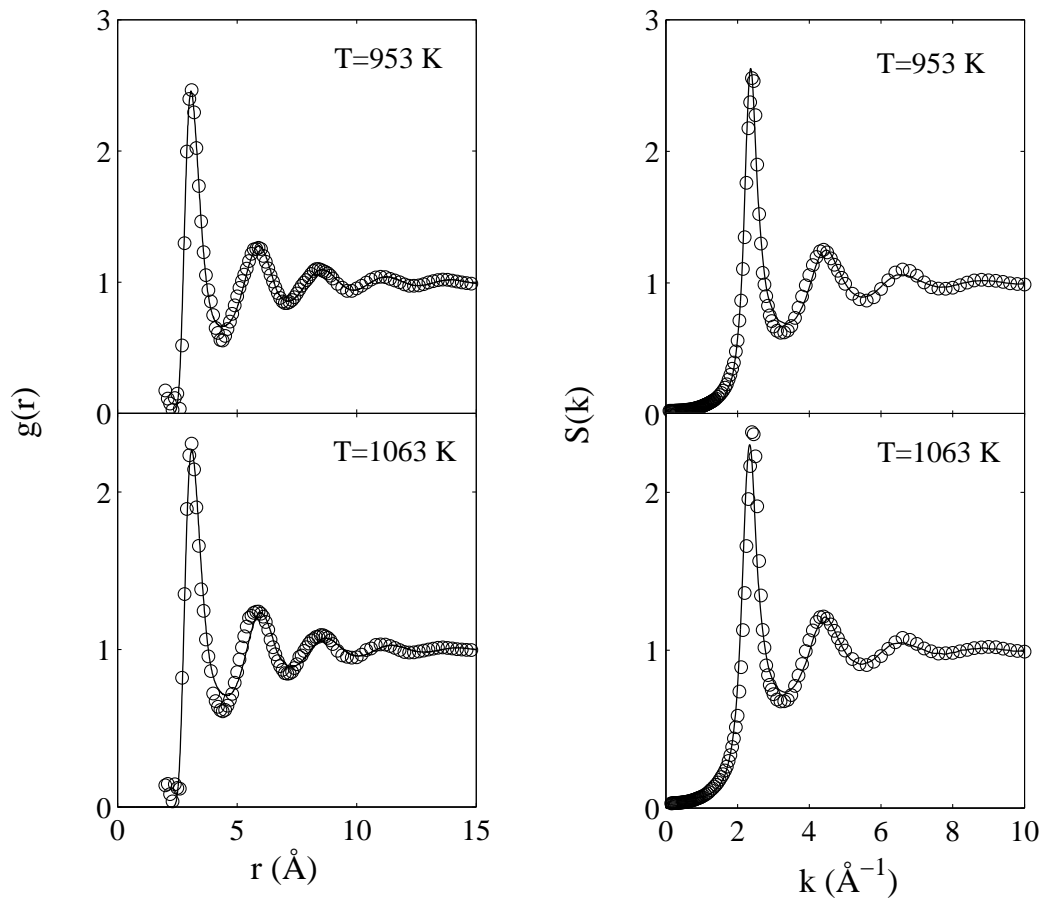
Figure 2. The equilibrium terms of liquid magnesium at the temperature $T = 953$ K and $T = 1063$ K (the radial distribution function of two particles, $g(r)$, and the static structure factor, $S(k)$): solid line − is the computer simulation molecular dynamics results; $(\circ \ \circ \ \circ)$ − is the experimental data on inelastic X-ray scattering [35, 36].

$$\Delta_k^{(4)} = \frac{\omega_k^{(8)} - \Delta_k^{(1)}\left[\left(\Delta_k^{(1)} + \Delta_k^{(2)}\right)^3 + 2\Delta_k^{(2)}\Delta_k^{(3)}\left(\Delta_k^{(1)} + \Delta_k^{(2)}\right) + \Delta_k^{(2)}\left(\Delta_k^{(3)}\right)^2\right]}{\Delta_k^{(1)}\Delta_k^{(2)}\Delta_k^{(3)}},$$

$$\ldots,$$

which connected with normalized frequency (spectral) moments $\omega_k^{(2m)}$ $(m = 1, 2, 3, ...)$ of the dynamic structure factor, $S(k, \omega)$ [20], i.e.

$$\omega_k^{(2m)} = \frac{\int_{-\infty}^{\infty} \omega^{2m} S(k, \omega) d\omega}{\int_{-\infty}^{\infty} S(k, \omega) d\omega} = \left.\frac{d^{2m}\phi_k(t)}{dt^{2m}}\right|_{t=0}. \tag{9}$$

In the framework of the definition (9) we can to find the microscopic expressions for the frequency moments $\omega_k^{(2i)}$, $i = 1, 2, 3, ...$,

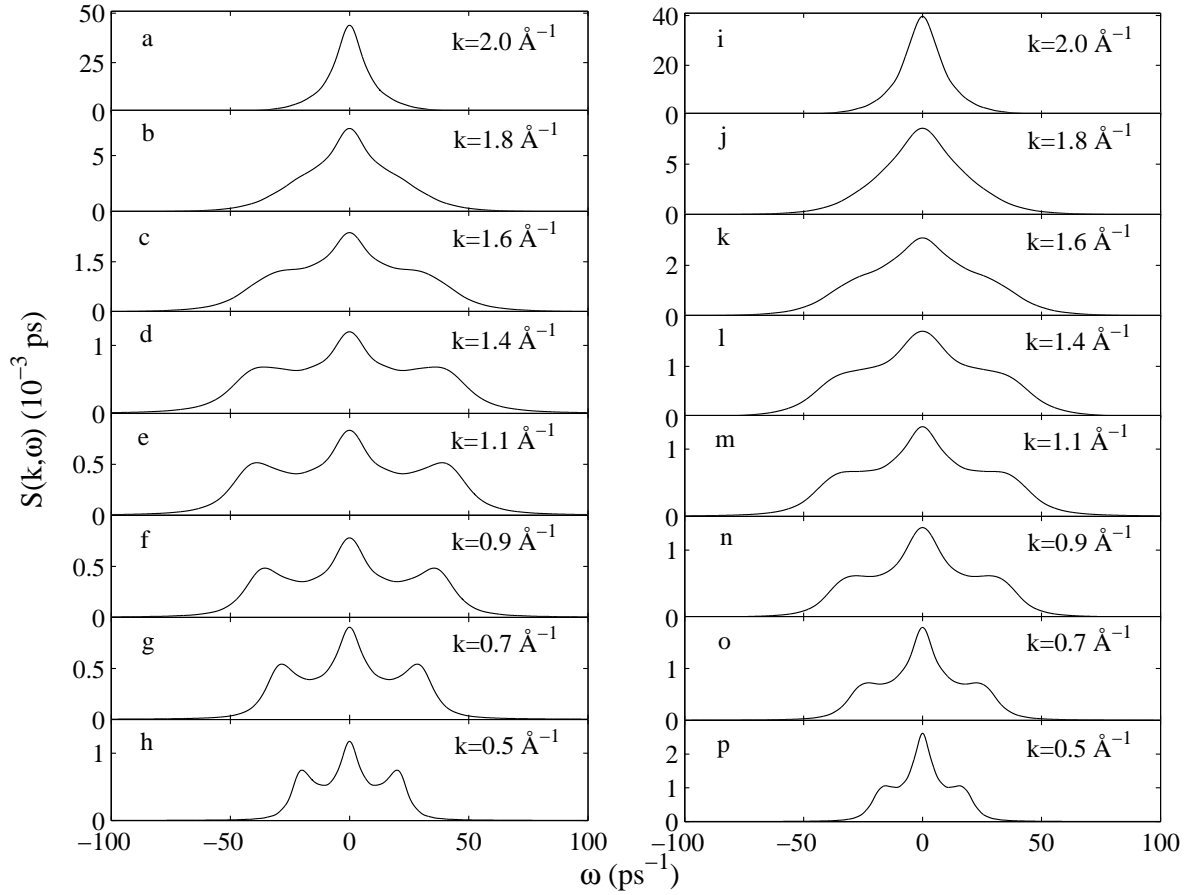$$\omega_k^{(2)} = \frac{k_B T}{m}\frac{k^2}{S(k)},$$

Figure 3. Dynamic structure factor, $S(k,\omega)$, of liquid magnesium which obtained from molecular dynamics computer simulation: (a-h) — at the temperature $T = 953$ K; (i-p) — at the temperature $T = 1063$ K.

$$\omega_k^{(4)} = 3\Delta_k^{(1)}\frac{k_B T}{m}k^2 + \frac{N k_B T}{m^2 V S(k)}k^2 \int d\mathbf{r} g(r)[1 - \cos(\mathbf{k r})]\nabla_l^2 E_{pot}(r),$$

$$\omega_k^{(6)} = 15\left(\frac{k_B T}{m}\right)^2 k^4 + \frac{N k_B T}{m^2 V}k^2 \int d\mathbf{r} g(r)\nabla_l^2 E_{pot}(r) + \quad\quad\quad (10)$$

$$+6\frac{N k_B T}{m^2 V}k \int d\mathbf{r} g(r)\nabla_l^3 E_{pot}(r)\sin(\mathbf{k r}) +$$

$$+2\frac{N}{m^2 V} \int d\mathbf{r} g(r)[\nabla\nabla_l E_{pot}(r)]^2 [1 - \cos(\mathbf{k r})] +$$

$$+\left(\frac{N}{mV}\right)^2 \int d\mathbf{r} d\mathbf{r}' g_3(\mathbf{r}, \mathbf{r}')(\nabla\nabla_l E_{pot}(r))(\nabla'\nabla_l' E_{pot}(r')),$$

$$\dots.$$

Here, subscript l to indicate on the longitudinal component, parallel vector $\mathbf{k}$, $g(r)$ – is the radial distribution function of two particles, $g_3(\mathbf{r}, \mathbf{r}')$ – is the three-particle distribution function, $E_{pot}(r)$ – is the interparticle potential, $k = |\mathbf{k}|$ – is the wave-number, k_B, T and m – are the Boltzmann coefficient, the temperature of the system and the atomic mass of magnesium, respectively. The expressions of the senior order frequency moments has very complicated view and contains many-particle distribution functions.
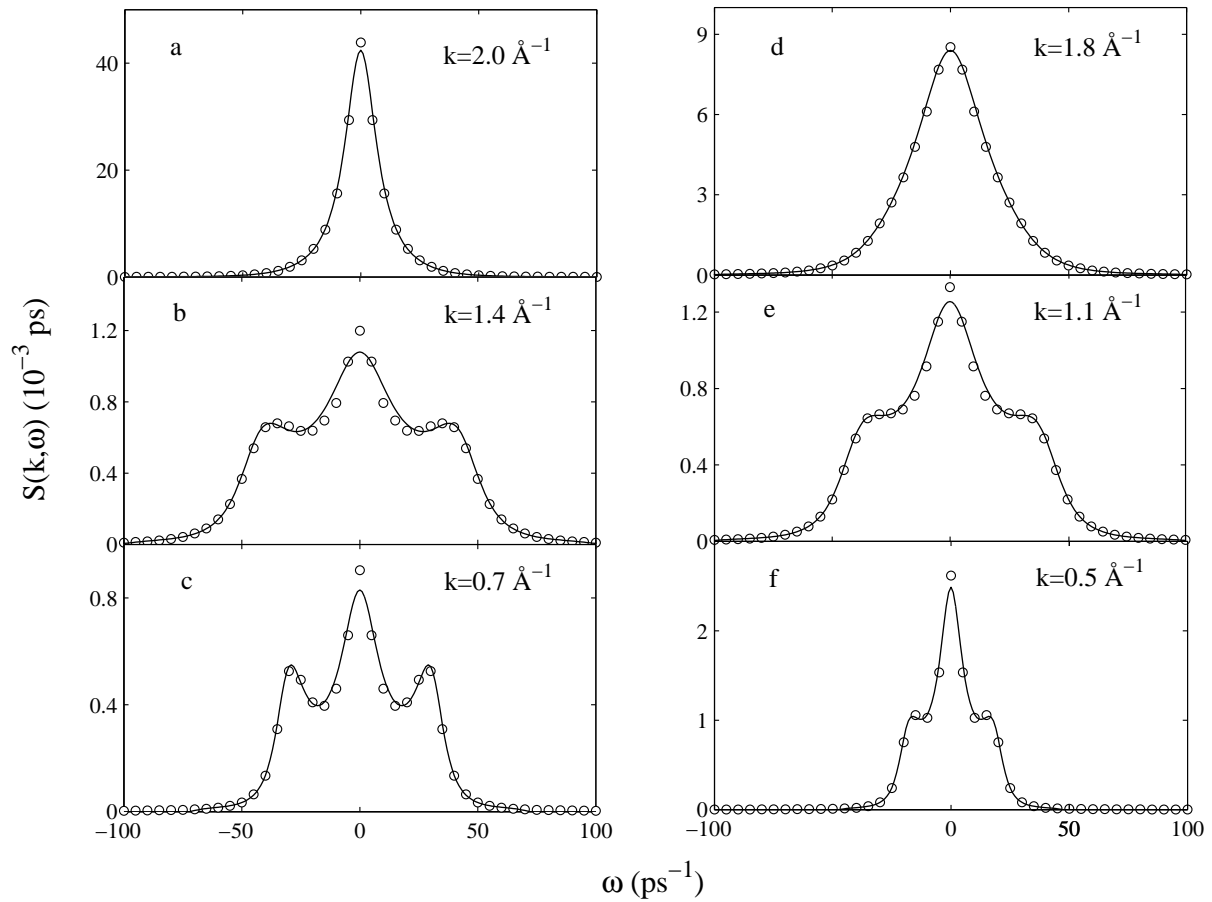
Figure 4. Dynamic structure factor of liquid magnesium at the temperatures $T = 953$ K (a-c) and $T = 1063$ K (d-f): ($\circ$ $\circ$ $\circ$) – are the computer simulation molecular dynamic data; solid line represent the results of the theoretical calculation by the equation (13).

The determination of analytic view of the TCF $\phi_k(t)$ [or its Laplace-transformation $\widetilde{\phi}_k(s)$] usually come to calculation the ith order memory function, $M_k^{(i)}(t)$, [or $\widetilde{M}_k^{(i)}(s)$] or search the method of closing of the infinite fraction (7). For closing of the equation (7) there were suggested different methods:

(i) the markoff approximation of the relaxation processes [21];

(ii) the model memory function method, when the ith order memory function $M_k^{(i)}(t)$ approximated some simple model function, for example, exponential or gaussian function, hyperbolic secant [22, 23, 24, 25, 26];

(iii) the mode-coupling method [27], when the second order memory function, $M_k^{(2)}(t)$, approximated polynomial of the initial time correlation function $\phi_k(t)$.

In this paper we develop new approach the based on N.N. Bogoliubov's ideas about reduced description of statistical systems and hierarchy of the relaxation time-scales [28], at the first time suggested in the work [29]. Recently, this approach successfully used for description of the dynamic structure factor spectra, $S(k, \omega)$, of liquid alkaline metals near its melting points, which observed in experiments on inelastic X-ray scattering [30], and coherent neutron scattering [31, 32]. In the framework of this approach, supposed, that on some of the relaxation level realized
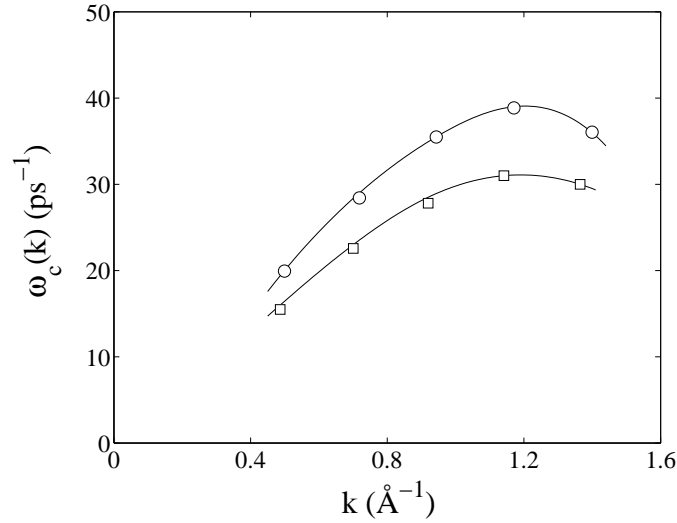
Figure 5. Dispersion of the high-frequency peak of the $S(k,\omega)$: computer simulation molecular dynamics results at the temperature $T = 953$ K and the numerical density $n = 0.0383$ Å^{-3} ($\circ \circ \circ$); ($\square \square \square$) – are the MD results at the temperature $T = 1063$ K ($n = 0.0355$ Å^{-3}); solid line presents the theoretical results by equation (13).

the equalization of the time scales of the two neighbor relaxation processes, i.e. $\tau_k^{(i)} = \tau_k^{(i+1)}$, where $\tau_k^{(i)} = \int_0^\infty dt M_k^{(i)}(t) = \widetilde{M}_k^{(i)}(s=0)$ – is the time correlation of the ith order memory function.

Applying this approach to the third relaxation level ($i = 3$) [29, 31] we obtained the expression for the third order memory function

$$\widetilde{M}_k^{(3)}(s) = \frac{-s + \sqrt{s^2 + 4\Delta_k^{(4)}}}{2\Delta_k^{(4)}}. \tag{11}$$

By substituting this expression in the equation (7) and taking into account the equation of the dynamic structure factor, $S(k,\omega)$, which interrelated with Laplace-transformation of the time correlation function of density fluctuation $\phi_k(t)$ [33]:

$$S(k,\omega) = \frac{S(k)}{\pi}\mathrm{Re}\widetilde{\phi}_k(s = i\omega) \tag{12}$$

we can to obtain the equation of form:

$$S(k,\omega) = \frac{S(k)}{2\pi}\Delta_k^{(1)}\Delta_k^{(2)}\Delta_k^{(3)}\sqrt{4\Delta_k^{(4)} - \omega^2}\left\{\left(\Delta_k^{(1)}\Delta_k^{(3)}\right)^2 + \omega^2\left[-2\Delta_k^{(1)}\left(\Delta_k^{(3)}\right)^2 + \right.\right.$$

$$+\left(\Delta_k^{(1)}\right)^2\Delta_k^{(4)} - \left(\Delta_k^{(1)}\right)^2\Delta_k^{(3)} + 2\Delta_k^{(1)}\Delta_k^{(2)}\Delta_k^{(4)} - \Delta_k^{(1)}\Delta_k^{(2)}\Delta_k^{(3)} + \left(\Delta_k^{(2)}\right)^2\Delta_k^{(4)}\right] +$$

$$+\omega^4\left[\left(\Delta_k^{(3)}\right)^2 - 2\Delta_k^{(1)}\Delta_k^{(4)} + 2\Delta_k^{(1)}\Delta_k^{(3)} - 2\Delta_k^{(2)}\Delta_k^{(4)} + \Delta_k^{(2)}\Delta_k^{(3)}\right] +$$

$$+\omega^6\left[\Delta_k^{(4)} - \Delta_k^{(3)}\right]\right\}^{-1}. \tag{13}$$

4. Conclusions and discussions

To study the structure and the equilibrium properties of liquid magnesium we calculated by MD the radial distribution function of two particles

$$g(r) = \frac{V}{4\pi r^2 N} \left\langle \sum_{j=1}^{N} \frac{\Delta n_j(r)}{\Delta r} \right\rangle \tag{14}$$

and the static structure factor

$$S(k) = \frac{1}{N} \left\langle \sum_{j=1}^{N} e^{-i\mathbf{k}\mathbf{r}_j(0)} \sum_{l=1}^{N} e^{i\mathbf{k}\mathbf{r}_l(0)} \right\rangle. \tag{15}$$

Where $\Delta n_j(r)$ – is the number of particles in the spherical layer Δr at the distance r from the jth particle. The calculation of the static structure factor, $S(k)$, with reliable precision on basis of the equation (15) usually take plenty computer time, therefore numerical computation of the $S(k)$ was executed on base of behavior of the radial distribution function of two particles $g(r)$ with the equation of form [34]:

$$S(k) = 1 + 4\pi n \int_0^\infty r^2 \Big(g(r) - 1\Big) \frac{\sin(kr)}{kr} dr. \tag{16}$$

Fig. 2 shows the functions of $g(r)$ and $S(k)$ for the liquid magnesium in comparison with the experimental data on inelastic X-ray scattering [35, 36]. From the figure we can to see, that the computer simulation molecular dynamics with the 'glue' interparticle potential for the equilibrium characteristics are in a good agreement with experimental data. Consequently, the potential given by Eq. (1) allow correctly to describe the microscopic structure of the liquid magnesium at the thermodynamic states near the melting point.

To study of the dynamic properties of the liquid magnesium we calculated the dynamic structure factor spectra, $S(k,\omega)$. In Fig. 3 we demonstrate the computer simulation molecular dynamics results for the dynamic structure factor, $S(k,\omega)$, of the liquid magnesium at the temperatures $T = 953$ K (Fig. 3 a-h) and $T = 1063$ K (Fig. 3 i-p) for eight wave-numbers, k, from 0.5 Å^{-1} to 2 Å^{-1}. From the figure we can to see that the positions and heights of the central and side peaks with increasing of the wave-number endure noticeable changes. High-frequency peaks in the dynamic structure factor spectra, which characterized collective dynamics of particles in liquid the most distinctly expressed in the wave-number region from 0.5 Å^{-1} to 1.6 Å^{-1}. At the values $k \geq 1.8$ Å^{-1}, which corresponding approximately position of the first maximum ($k \sim 2$ Å^{-1}) in the structure factor, $S(k)$, these peaks entirely disappear. Therefore, high-frequency collective excitations are observed only on the spatial scales ($r \sim 2\pi/k$), corresponding interatomic distances.

In Fig. 4 presents the theoretical results [equation of (13)] for the dynamic structure factor spectra, $S(k,\omega)$, (solid line) are compared with molecular dynamics data (○ ○ ○). The theoretical results of $S(k,\omega)$ are seen to precisely reproduce the molecular dynamics computer simulation data at the temperatures $T = 953$ K (Fig. 4 a-c) and $T = 1063$ K (Fig. 4 d-f) for the whole studied wave-number region. A small discrepancy between the theory and the MD data, which observed in the low-frequency region of the $S(k,\omega)$, are connected with errors in the Fourier-transformation of the time correlation function of density fluctuations, $\phi_k(t)$, on the long-time asymptotic. Frequency relaxation parameters $\Delta_k^{(i)}$ (где $i = 1, 2, 3$), which contains in the equation (13), were computed by equations (8) and (10). Fourth frequency parameter $\Delta_k^{(4)}$ was obtained from comparison the theory and the molecular dynamics data. About good qualitative and quantitative agreement for the both thermodynamic states of liquid magnesium we can also to judge on the dispersion of the high-frequency peak $\omega_c(k)$, which is presented in Fig. 5.

The results of this brief report can be summarized as follows:

(i) The 'glue' interparticle potential [18] allows adequately to describe the microscopic structure and dynamics of magnesium particles at the thermodynamic states with the temperatures $T = 953$ K and $T = 1063$ K;

(ii) In the spectra of the dynamic structure factor near and above the melting point are observed the high-frequency excitements in the wave-number region k to the point of 1.6 Å^{-1}, corresponding the spatial scales and the lengths ($r \sim 2\pi/k$), which are comparable with the interparticle distances;

(iii) The theoretical model of the dynamic structure factor, developed on the N.N. Bogoliubov's ideas about the reduced description of statistical systems and hierarchy of the relaxation time scales in the framework of the Zwanzig-Mori's memory function formalism, allows correctly to describe the relaxation processes and collective dynamics of the liquid magnesium on the picosecond time scales and in the microscopic space regions.

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