

# Self-consistent approach in microdynamics description of supercooled liquids and glasses

© A.V. Mokshin, R.M. Yulmetyev, R.M. Khusnutdinov, P. Hänggi\*

Tatar State Humanitarian-Pedagogical University,  
420021 Kazan, Russia

\* Department of Physics, University of Augsburg,  
D-86135 Augsburg, Germany

E-mail: mav@theory.kazan-spu.ru

(Received December 13, 2005)

The study of the microdynamics of supercooled liquids and glasses is executed through calculations of the dynamic structure factor  $S(k, \omega)$ . The theory developed on the basis of a self-consistent approach in the framework of memory function formalism is applied to define the frequency spectra  $(m/k_B T)S(k, \omega)$  of supercooled argon at the temperature  $T = 5$  K for wave number region from 2 to  $8.5 \text{ nm}^{-1}$ . Obtained results are in a good agreement with the molecular dynamics simulation data.

This work was partially supported by the Russian Ministry of Education and Science (grant № 03-06-00218a) and RFBR (№ 02-02-16146).

PACS: 62.60.+v, 47.11.-j, 62.10.+s, 6120.Gy

The understanding of the microscopic dynamics of supercooled liquids and of its relation with the glass transition is one of the open problems in the physics of the condensed matter, which induces the performance of numerous experimental [1–3] and theoretical investigations [4]. Although different details of the microdynamics of supercooled liquids and glasses are essentially exactly determined, much is unclear still now. So, for example, even though the relation between the phenomenology of glass transition and the long time dynamics has been almost clarified, the effect of „the structural arrest“ on the high frequency collective vibrational motion and a role of memory effects in structural relaxation is much less clear [5–7]. The present paper is devoted to the study of this issue.

The most convenient way to study the dynamics of the density fluctuations is the determination of the dynamic structure factor  $S(k, \omega)$ , which can be experimentally obtained by means of the scattering of light, neutrons and X-rays. One of the common features established for glass and supercooled liquids via the above-mentioned experimental techniques consists in the fact that acoustic-like excitations in these systems are propagated up to a value of the wave number  $k$ , which corresponds to the minimal interparticle distances. As this takes place, the broadening of high frequency peaks corresponded to these collective excitations follows a power law  $Dk^2$ , where  $D$  does not depend practically on temperature. It is need to note that similar features were earlier established in the microdynamics of density fluctuations in liquid alkali metals [8–10]. From the theoretical point of view,  $S(k, \omega)$  can be found from the generalized Langevin equation [11] for the normalised density correlator  $\phi(t) = \langle \delta\rho_k(t)\delta\rho_{-k}(0) \rangle / \langle |\delta\rho_k(0)|^2 \rangle$

$$\frac{d^2\phi(k, t)}{dt^2} + \Omega_1^2(k)\phi(k, t) + \Omega_2^2(k) \int_0^t d\tau M_2(k, t - \tau) \frac{d\phi(k, \tau)}{d\tau} = 0, \quad (1)$$

where  $M_2(k, t)$  is the second order memory function,  $\Omega_1^2(k)$  and  $\Omega_2^2(k)$  are the frequency relaxation parameters, which are expressed through the even frequency moments of  $S(k, \omega)$

$$\omega^{(n)}(k) = \frac{\int d\omega \omega^n S(k, \omega)}{\int d\omega S(k, \omega)}. \quad (2)$$

Namely,

$$\Omega_1^2(k) = \omega^{(2)}(k) = \frac{k_B T}{m} \frac{k^2}{S(k)}, \quad (3)$$

$$\Omega_2^2(k) = \frac{\omega^{(4)}(k)}{\omega^{(2)}(k)} - \omega^{(2)}(k). \quad (4)$$

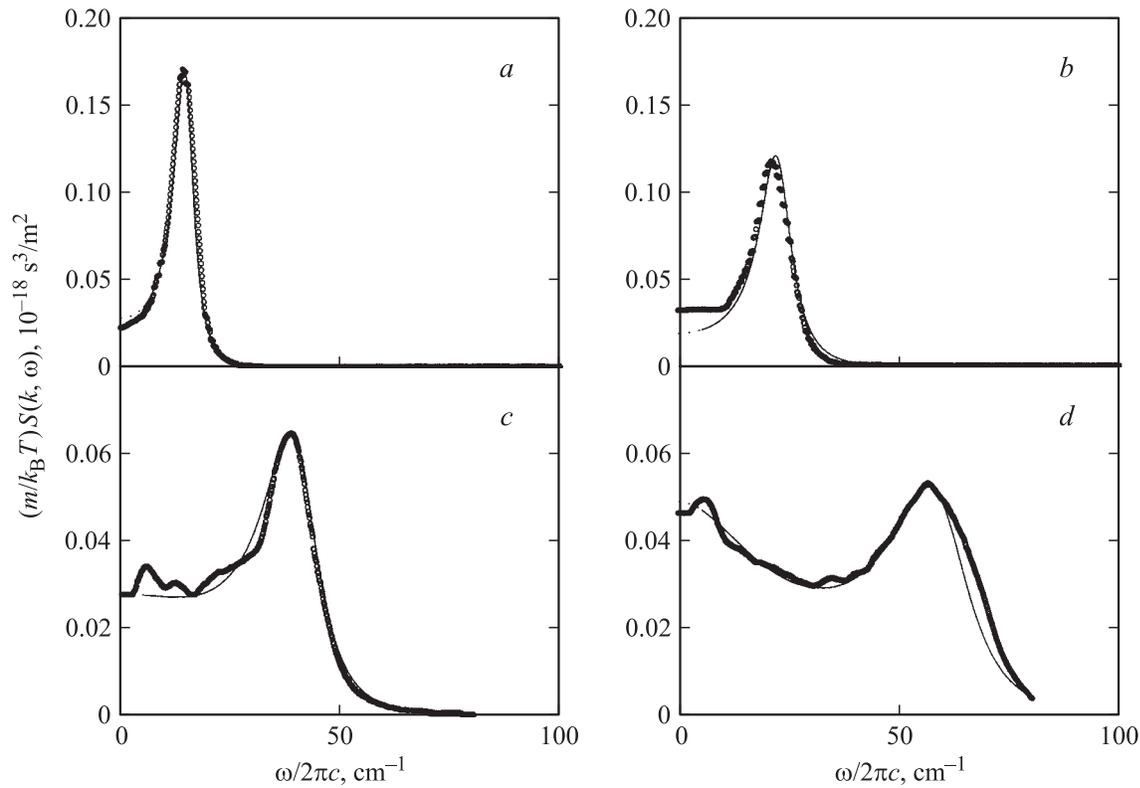
As was recently shown (see Ref. [7], and Eq. (7) in Ref [12]), the Laplace transform,  $\tilde{f}(s) = \int_0^\infty e^{-st} f(t) dt$ , of the non-Markovian equation (1) for the case of non-ergodicity glass systems allows one to obtain the dynamic structure factor in the following form

$$S(k, \omega) = S(k) \left[ f(k)\delta(\omega) + \frac{1 - f(k)}{\pi} \times \frac{[\Omega_1^2(k) + \Omega_2^2(k)]M_2'(k, \omega)}{[\omega^2 - \Omega_1^2(k) + \omega\Omega_2^2(k)M_2''(k, \omega)]^2 + [\omega\Omega_2^2(k)M_2'(k, \omega)]^2} \right], \quad (5)$$

where  $\tilde{M}_2(k, i\omega) = M_2'(k, \omega) + iM_2''(k, \omega)$ ,  $S(k) = \langle |\delta\rho_k(0)|^2 \rangle$  is the static structure factor, and  $f(k)$  is the non-ergodicity factor, which is expressed thorough  $\Omega_1^2(k)$  and  $\Omega_2^2(k)$  [4,6]

$$f(k) = \lim_{t \rightarrow \infty} \phi(k, t) = \mathcal{F}(\Omega_1^2(k), \Omega_2^2(k)). \quad (6)$$

Then, the problem of definition of the dynamic structure factor  $S(k, \omega)$  is reduced to the finding of the second-order memory function  $M_2(k, t)$  (or its the Laplace transform),



**Figure 1.** Frequency spectra of  $(m/k_B T)S(k, \omega)$  of supercooled argon for  $T = 5$  K at  $k = 2.0$  (a),  $2.9$  (b),  $5.0$  (c), and  $8.5 \text{ nm}^{-1}$  (d). Circles are the data of molecular dynamics simulations [6], solid line is our theoretical results.

which is also the time correlation function described the corresponding relaxation process. From the point of view of the Zwanzig–Mori formalism [13,14], the Laplace transforms of the whole set of memory functions arisen in hierarchical chain of the non-Markovian equations, interrelate by the following recurrent relation

$$\tilde{M}_n(k, s) = [s + \Omega_{n+1}^2(k)\tilde{M}_{n+1}(k, s)]^{-1}, \quad (7)$$

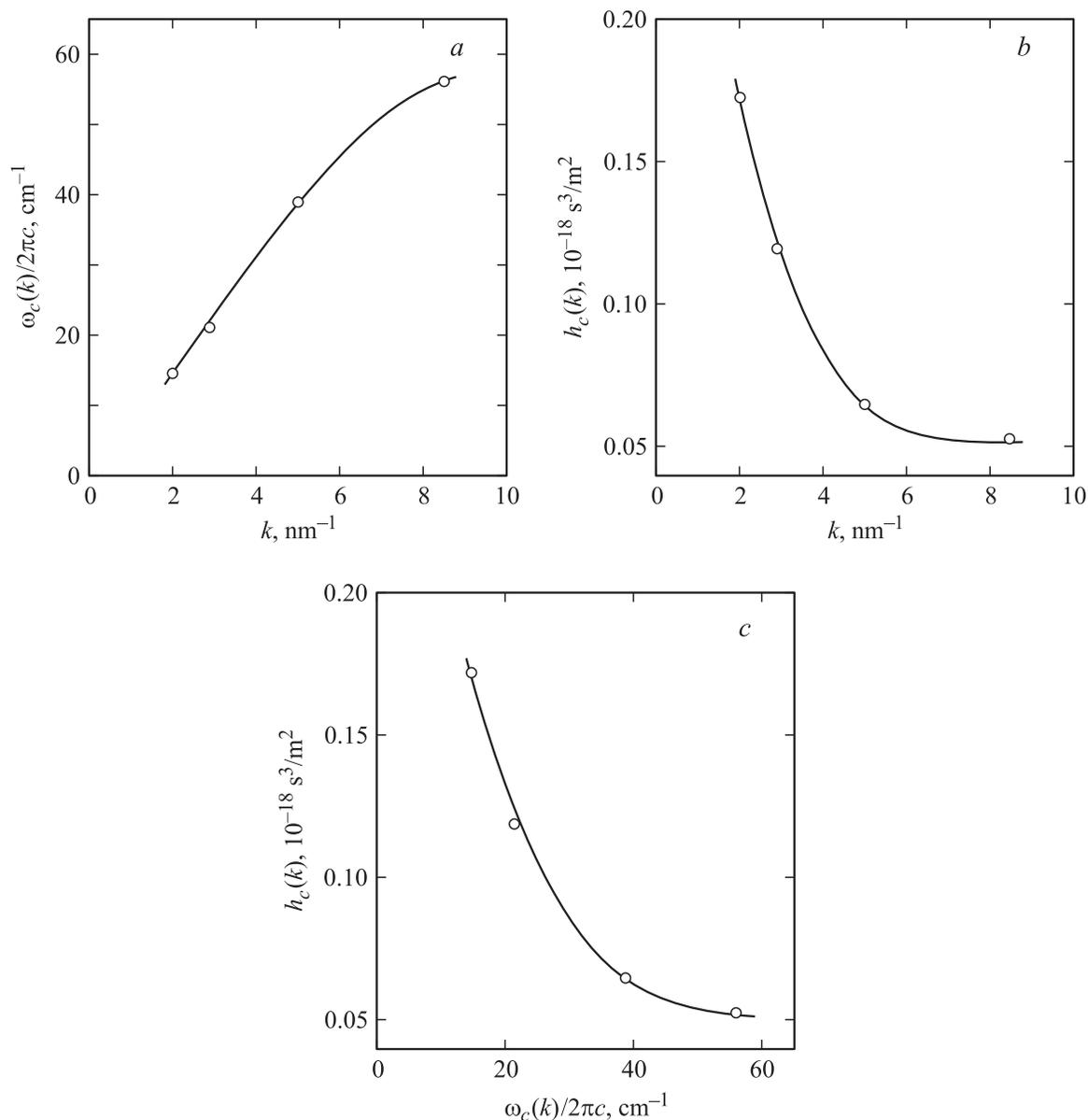
where  $\Omega_n^2(k)$  is the relaxation parameter of the  $n$  the order. The finding of the term  $M_2(k, t)$  can be also executed in the framework of a self-consistent approach based on the assumption about equalization of time-scales of high-order memory functions,  $\tau_3(k)$  and  $\tau_4(k)$ , where  $\tau_n(k) = \int_0^\infty dt M_n(k, t)$  [8].<sup>1</sup> As a result, we obtain the termination in the recurrent relation (7) and find exactly the following expression for  $M_2(k, t)$  without any trivial approximations for the memory function  $M_2(k, t)$  (or  $\tilde{M}_2(k, s)$ ) by different model time (frequency) dependencies

$$\tilde{M}_2(k, s) = \left[ s + \frac{\Omega_3^2(k)\sqrt{s^2 + 4\Omega_4^2(k) - \Omega_3^2(k)s}}{2\Omega_4^2(k)} \right]. \quad (8)$$

Now, the spectra  $S(k, \omega)$  can be deduced by simple substitution of Eq. (8) into Eq. (5). So, the position as well

<sup>1</sup> Such interrelation between  $\tau_3(k)$  and  $\tau_4(k)$  is based on the assumption of equalization of time scales for TCF of energy current fluctuations and its memory function.

as broadening and the amplitude of high frequency peak of  $S(k, \omega)$  in this approach are interrelated terms, which are determined by the frequency relaxation parameters  $\Omega_3^2(k)$  and  $\Omega_4^2(k)$ . It is need to note that as it was recently shown in Ref. [15], this approach allows one to obtain the second order memory function in terms of simple relaxation functions. It is in a full agreement with the mode-coupling theory ideas [16]. In accordance with the presented approach, the spectra of the dynamic structure factor  $S(k, \omega)$  were calculated by Eqs. (5) end (8) for the supercooled argon at temperature  $T = 5$  K for wave numbers  $k = 2.0, 2.9, 5.0$  and  $8.5 \text{ nm}^{-1}$ . The parameter  $\Omega_1^2(k)$  was exactly found from Eq. (3), whereas numerical values of the second order relaxation parameter  $\Omega_2^2(k)$  were taken from Ref. [6]. The frequency parameters  $\Omega_3^2(k)$  and  $\Omega_4^2(k)$  were determined from the comparison of theoretical results with the molecular dynamics simulation data. Obtained theoretical results for the reduced dynamical structure factor  $(m/k_B T)S(k, \omega)$  (solid line) together with the results of the molecular dynamics simulation (circles) [6] are presented in Fig. 1. It is need to note that the molecular dynamics study of Ref. [6] was performed for system of  $N = 2048$  argon atoms interacted *via* a Lennard–Jones potential ( $\epsilon/k_B = 125.2 \text{ K}$ ,  $\sigma = 3.405 \text{ \AA}$ ). It is obvious that theoretical curves are in a good agreement with the molecular dynamics curves data for the whole range of wave number values. Insignificant oscillations observed in the data of molecular dynamics simulations for low frequency regions



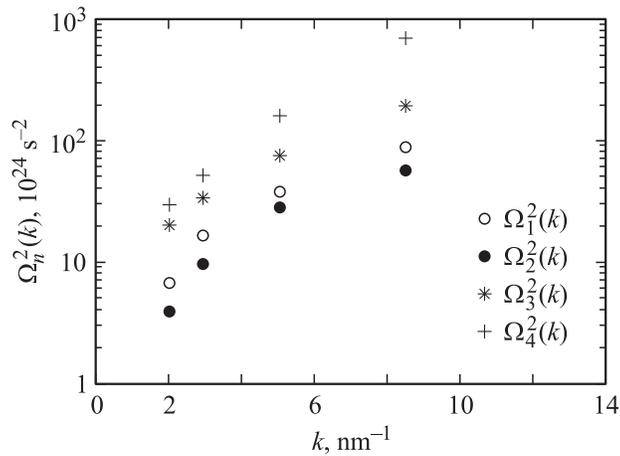
**Figure 2.** (a) dispersion of the side peak of the dynamic structure factor for supercooled argon ( $T = 5$  K); (b)  $k$ -dependence of the side peak amplitude; (c) dependence of the side peak amplitude  $h_c$  on the frequency of collective excitations  $\omega_c/2\pi c$ . Solid line presents theoretical results, circles are the data of molecular dynamics simulations [6].

of dynamic structure factor spectra are related to errors, which arise at the numerical Laplace- (Fourier-) transform of data for the density correlator [6]. A good agreement between theory and molecular dynamics simulation data are also seen in Fig. 2, where dispersion of high frequency peak of dynamic structure factor (see Fig. 2, a), dependencies of the side peak amplitude  $h_c$  on the wave number  $k$  (see Fig. 2, b) and on the frequency  $\omega_c/2\pi c$  at fixed values of  $k$  (see Fig. 2, c) are presented. In Fig. 3, we present numerical values of frequency relaxation parameters  $\Omega_n^2(k)$ ,  $n = 1, 2, 3$  and 4, used in our calculations. It is need here to note that all frequency relaxation parameters have the same  $k$ -dependence. Similar scenario was earlier obtained for the description of microscopic dynamics of liquid alkali metals

(lithium, sodium, rubidium and caesium) near their melting temperatures [8–10,15].

In conclusion, this paper is devoted to the development of a self-consistent approach executed in the framework of memory function formalism and suggested earlier for the description of microdynamics of liquid alkali metals for finding the dynamic structure factor of supercooled liquids. The results of the theoretical analysis of  $S(k, \omega)$  performed for supercooled argon at the temperature  $T = 5$  K for values of wave numbers ranging from 2 to  $8.5 \text{ nm}^{-1}$  are in a good agreement with molecular dynamics simulation data. It allows us to make the following inferences.

1) Possibility of the use of quasi-hydrodynamic approach to the description of „instantaneous“ dynamical processes in



**Figure 3.** Frequency relaxation parameters  $\Omega_n^2(k)$ ,  $n = 1, 2, 3$  and 4, used in theoretical analysis of  $S(k, \omega)$  for supercooled argon at  $T = 5$  K.

supercooled liquids and glasses at the  $10^{-12}$  s time scale in the microscopic spatial space.

2) Microscopic processes and corresponding collective excitations, which are observed in the THz frequency region of the dynamic structure factor spectra, have unified origin in liquid alkali metals as well as in supercooled liquids that can serve as a convincing proof for the benefit of the assumptions of Ref. [17].

The authors acknowledge V. Götze, M. Sperl and V.Y. Shurygin for the useful correspondence.

## References

- [1] A. Matic, L. Börjesson, G. Ruocco, C. Masciovecchio, A. Mermet, F. Sette, R. Verbeni. *Europhys. Lett.* **54**, 1, 77 (2001).
- [2] C. Masciovecchio, G. Monaco, G. Ruocco, F. Sette, A. Cunsolo, M. Krisch, A. Mermet, M. Soltwisch, R. Verbeni. *Phys. Rev. Lett.* **80**, 544 (1998).
- [3] D. Fioretto, U. Buchenau, L. Comez, A. Sokolov, C. Masciovecchio, A. Mermet, G. Ruocco, F. Sette, L. Willner, B. Frick, D. Richter, L. Verdini. *Phys. Rev. E* **59**, 4470 (1999).
- [4] W. Götze. *Liquids, freezing, and the glass transition* / Eds J.P. Hansen, D. Levesque, J. Zinn-Justin. North-Holland, Amsterdam (1991).
- [5] A.V. Mokshin, R.M. Yulmetyev, P. Hänggi. *Phys. Rev. Lett.* **95**, 200601 (2005).
- [6] G. Ruocco, F. Sette, R. Di Leonardo, G. Monaco, M. Sampoli, T. Scopigno, G. Viliani. *Phys. Rev. Lett.* **84**, 5788 (2000).
- [7] G. Ruocco, F. Sette. *J. Phys.: Cond. Matter* **13**, 9141 (2001).
- [8] R.M. Yulmetyev, A.V. Mokshin, P. Hänggi, V.Yu. Shurygin. *Phys. Rev. E* **64**, 057101 (2001).
- [9] R.M. Yulmetyev, A.V. Mokshin, P. Hänggi, V.Yu. Shurygin. *JETP Lett.* **76**, 147 (2002).
- [10] R.M. Yulmetyev, A.V. Mikshin, T. Scopigno, P. Hänggi. *J. Phys.: Cond. Matter* **15**, 2235 (2003).
- [11] U. Balucani, M. Zoppi. *Dynamics of the liquid state*. Clarendon Press, Oxford (1994).

- [12] S. Mossa, G. Monaco, G. Ruocco, M. Sampoli, F. Sette. *J. Chem. Phys.* **116**, 1077 (2002).
- [13] R. Zwanzig. *Phys. Rev.* **124**, 1338 (1961).
- [14] H. Mori. *Prog. Theor. Phys.* **33**, 423 (1965).
- [15] A.V. Mokshin, R.M. Yulmetyev, P. Hänggi. *J. Chem. Phys.* **121**, 7341 (2004).
- [16] S.P. Das. *Rev. Mod. Phys.* **76**, 785 (2004).
- [17] T. Scopigno, G. Ruocco, F. Sette, G. Monaco. *Science* **302**, 849 (2003).