



## Short Communication

## Anomalous behavior of dispersion of longitudinal and transverse collective excitations in water

Yu.D. Fomin\*, E.N. Tsiok, V.N. Ryzhov, V.V. Brazhkin

Institute for High Pressure Physics RAS, 108840 Kaluzhskoe shosse, 14, Troitsk, Moscow, Russia

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## ABSTRACT

We have studied the dependence of the excitation frequency of water along an isochore and an isotherm crossing the region of density anomaly. We have shown that the frequency of longitudinal excitations demonstrated anomalous temperature dependence along the isochore. At the same time the dependence of both longitudinal and transverse excitation frequencies on the density along the isotherm was very modest or even negligible in a fairly wide range of densities. This kind of behavior also seems anomalous in comparison with ordinary liquids.

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## 1. Introduction

Collective excitations are of great importance in solid-state physics [1,2]. Many properties of solids can be efficiently described on the basis of collective excitations, i.e. phonons. Only recently it has been recognized that collective excitations are of the same importance for liquids [3,4]. In particular, a phonon based theory of liquid thermodynamics was discussed in a recent review [5] (see also [6] for successful calculations of liquid specific heat based on a collective mode approach).

Although it has been widely known for a long time that viscous liquids can demonstrate phonon-like excitations similar to the ones in crystals, detailed investigation of collective excitations in liquids started only several decades ago. The reason for this is that experimental study of longitudinal and in particular transverse waves in liquids requires very high quality X-ray or neutron installations which became available only recently. Currently, high quality experimental data is available for several liquid metals [7–13], ionic solutions [14–16], and water [17,18].

Several theoretical models were proposed to describe collective excitation in liquids. Good agreement with experimental data was obtained in the model based on a representation of the dynamical structure factor as an infinite fraction introduced in Ref. [19] (see also [20–24] for examples of successful implementation of this model).

Collective excitations in liquids were also widely studied by means of computer simulation methods. The first attack on the problem was made in a classical set of papers by D. Levesque and L. Verlet [25]. After that numerous papers appeared in the literature where collective excitations in different liquids were studied using computer simulation methods.

It is well known that some liquids demonstrate unusual properties commonly called anomalies. The most well-known anomalous liquid is water which demonstrates more than 70 anomalies, such as density, diffusion, structural anomalies and many others [26]. In particular, there are some anomalies of thermodynamic properties, such as density anomaly, i.e. a negative thermal expansion coefficient. In solids it is well known that in the case of negative thermal expansion coefficients there are some phonon branches which demonstrate unusual density dependence: while in a normal crystal the phonon frequency increases with density, in the case of negative thermal expansion some phonon branches have a frequency which decreases with a density increase [27]. Because of this one can expect that the frequency of collective excitations of liquids with a density anomaly will also demonstrate unusual behavior.

This assumption was confirmed in our previous work where we studied the dispersion curves of the longitudinal excitation frequency along the isochores which crossed the region of the density anomaly [28]. It was found that while in normal liquid the frequency increased with temperature, the excitation frequency of the liquid with a density anomaly could decrease. An excitation frequency increase upon isochoric heating in normal liquids can be understood from the temperature dependence of the adiabatic speed of sound: in normal liquid it increases with temperature along the isochore. Interestingly, in anomalous liquids the qualitative behavior of the speed of sound remains the same, while the excitation frequency can decrease with temperature, which leads to the complex temperature dependence of positive sound dispersion (PSD), the phenomenon of the excitation frequency exceeding Debye values  $c_s k$ , where  $c_s$  is the adiabatic speed of sound and  $k$  is the magnitude of the wave-vector.

In the present paper we extended the findings of Ref. [28]. We performed a simulation of dispersion curves of water along isochores and isotherms crossing the density anomaly region and monitored the

\* Corresponding author.

E-mail address: [fomin314@mail.ru](mailto:fomin314@mail.ru) (Y.D. Fomin).

temperature and density dependence of the excitation frequency. We show that in both cases the behavior of the excitation frequency is anomalous.

### 2. System and methods

In the present paper we simulated water in an SPC/E model [29]. Although this model is not very accurate [30,31], it gives a correct qualitative description of the main anomalous features of water. At the same time the SPC/E model is computationally cheaper than more accurate ones, for instance, TIP4P/2005. Because of this we chose to study the SPC/E water model for rapid evaluation of the qualitative features of water behavior.

The maximum density temperature (TMD) of the SPC/E water model at atmospheric pressure is 241 K [31]. Because of this we simulated water along isotherm  $T = 240$  K in order to cross the density anomaly region. The density was varied from  $\rho_{min} = 0.95$  g/cm<sup>3</sup> up to  $\rho_{max} = 1.05$  g/cm<sup>3</sup>. Another set of simulations was along isochore  $\rho = 1.01$  g/cm<sup>3</sup>. The temperature was changed from  $T_{min} = 220$  K up to  $T_{max} = 700$  K.

In all cases we performed molecular dynamics simulations of 4000 water molecules in a cubic box with periodic boundary conditions. The initial structure is a high temperature structure at a given density. The system was equilibrated for  $1 \cdot 10^7$  steps with time step  $dt = 1$  fs. After that the system was simulated for another  $5 \cdot 10^7$  steps with  $dt = 0.1$  f. for calculating averages. This interval was divided into 10 blocks and then the results of all blocks were averaged.

In order to find the excitation frequencies of water we calculated the correlation functions of fluxes of the velocity current. The longitudinal and transverse parts of these correlation functions are defined as follows

$$C_L(k, t) = \frac{k^2}{N} \langle J_z(\mathbf{k}, t) \cdot J_z(-\mathbf{k}, 0) \rangle \tag{1}$$

and

$$C_T(k, t) = \frac{k^2}{2N} \langle J_x(\mathbf{k}, t) \cdot J_x(-\mathbf{k}, 0) + J_y(\mathbf{k}, t) \cdot J_y(-\mathbf{k}, 0) \rangle \tag{2}$$

where  $J(\mathbf{k}, t) = \sum_{j=1}^N \mathbf{v}_j e^{-i\mathbf{k}\mathbf{r}_j(t)}$  is the velocity current and wave vector  $\mathbf{k}$  is directed along the z axis [32,33]. The excitation frequencies are calculated as the location of the peak of the Fourier transform of these functions. The same methodology was successfully employed to investigate collective excitations in many different systems, for instance, liquid metals (see, for instance, Refs. [19–24, 34], supercritical metals [35], binary mixtures [36], molecular liquids [37], and many others).

In the present work we calculated the dispersion curves of the SPC/E water model along isochore  $\rho = 1.01$  g/cm<sup>3</sup> and isotherm  $T = 240$  K and monitored the evolution of the excitation frequency with temperature and density respectively. In the case of simple liquids the frequency increases both under isochoric heating and isothermal compression. As shown in our previous publication [28] anomalous liquids can demonstrate an anomalous decrease in the frequency when the temperature is increased at constant density. By analogy with crystals with a negative thermal coefficient [27] we may expect that anomalous behavior of the frequency of transverse excitations can take place in the water density anomaly region.

All simulations were performed in the LAMMPS simulation package [38].

### 3. Results and discussion

We start the discussion from the dispersion curves at  $\rho = 1.01$  g/cm<sup>3</sup> and different temperatures. Fig. 1 shows the dispersion curves of longitudinal (panel a) and transverse (panel b) excitations. One can see that

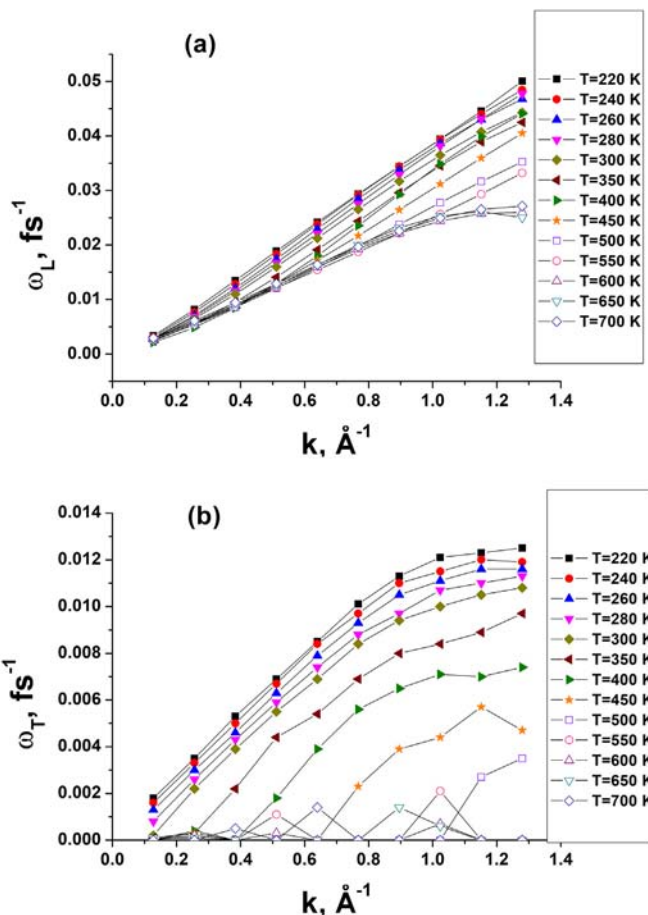


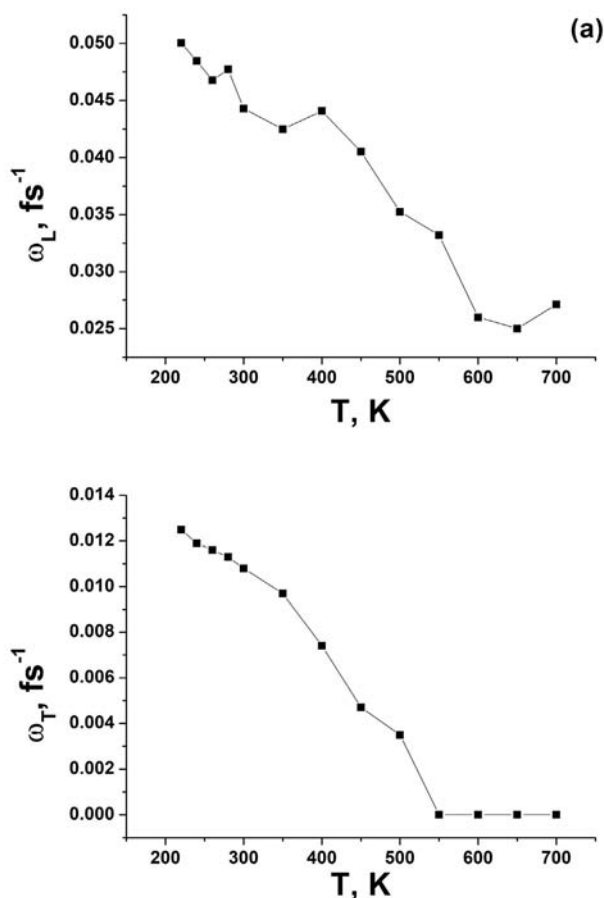
Fig. 1. The dispersion curves of the SPC/E water model along isochore  $\rho = 1.01$  g/cm<sup>3</sup>. Panel (a) shows the dispersion of longitudinal excitations, while panel (b) that of transverse excitations.

as the temperature increases the curves of longitudinal excitations go downward, i.e. the frequency decreases. Therefore, the system does demonstrate the anomalous dependence of the excitation frequency. Only at temperature as high as 700 K the curves undergo inversion of normal behavior, i.e. the frequency increases.

The frequency of transverse excitations also decreases at all temperatures. However, for transverse waves this is normal behavior. Transverse excitations take place in liquids close to the melting line. When temperature increases they disappear at the Frenkel line (FL) [39–41]. The Frenkel line for the SPC/E model was calculated in Ref. [42] (see also [43] for the Frenkel line of the TIP4P/2005 model of water). For  $\rho = 1.01$  g/cm<sup>3</sup> the FL temperature is about 500 K. From 1 (b) one can see that only two points close to the boundary of the Brillouin zone remain while at  $T = 550$  K no transverse waves are observed. Therefore, our study is consistent with previous calculations of the Frenkel line of the SPC/E water model.

In order to make the effect clearer we show the temperature dependence of the excitation frequency at a constant magnitude of the wave vector. Fig. 2 shows the temperature dependence of the excitation frequency of longitudinal and transverse excitations at  $k = 1.28 \text{ \AA}^{-1}$  which is the largest wave vector in our study. This value of  $k$  is selected since it is the closest one to the boundary of the Brillouin zone. In spite of noisy behavior the tendency of the longitudinal frequency to decrease with a temperature increase is apparent. Only at temperatures as high as 650–700 K the frequency starts to increase.

In the case of transverse excitations the situation is typical for liquid. Liquids demonstrate some shear rigidity at low temperature. However,



**Fig. 2.** The temperature dependence of the excitation frequency at fixed wave vector  $k = 1.28 \text{ \AA}^{-1}$  along  $\rho = 1.01 \text{ g/cm}^3$ . (a) The frequency of longitudinal excitations, (b) that of transverse excitations.

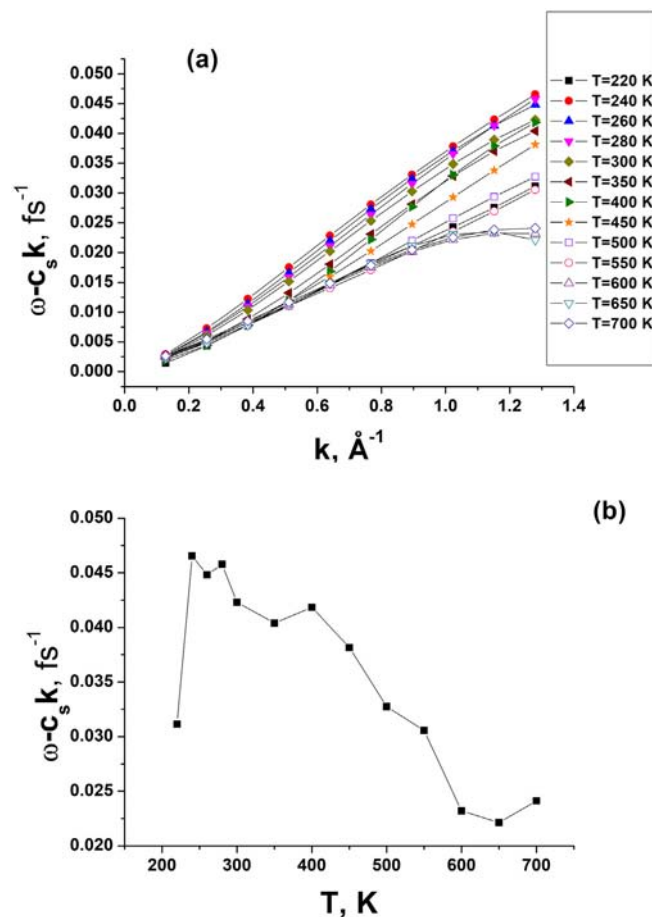
rigidity decreases with temperature, and therefore transverse excitations become depressed and finally disappear. This is exactly what we observe in the present case.

It is also instructive to study the behavior of PSD in the system. One can say that the system demonstrates positive sound dispersion at wave-vector  $k$  if  $\omega_l(k) > c_s k$ , where  $c_s$  is the adiabatic speed of sound. In the case of anomalous liquid the speed of sound increases upon isochoric heating, while the frequency of longitudinal excitations may decrease. It leads to the non-monotonous dependence of PSD in the system.

In order to study PSD in the system we consider the quantity  $\omega_l(k) - c_s k$ . If this quantity is positive, then the system demonstrates PSD. The difference defined above at isochore  $\rho = 1.01 \text{ g/cm}^3$  is shown in Fig. 3 (a). One can see that all curves are positive, which means that water demonstrates very strong PSD. To make the temperature dependence of PSD more visible we show the temperature dependence of  $\omega_l(k) - c_s k$  at the largest wave-vector in this study  $k = 1.28 \text{ \AA}^{-1}$  (Fig. 3(b)). One can see that the magnitude of PSD decreases with a temperature increase. However, even at temperature as high as 700 K PSD is still about 2.5%. Such strong PSD is in qualitative agreement with experimental data for water [18].

Let us consider the dispersion curves at isotherm  $T = 240 \text{ K}$  and different densities (Fig. 4). We see that the effect of density on the frequency of longitudinal excitations is very modest. From the inset of panel (a) we see that the frequencies of the last points of the curves at  $\rho = 0.95 \text{ g/cm}^3$  and  $1.05 \text{ g/cm}^3$  are  $\omega_{0.95} = 0.0458 \text{ fs}^{-1}$  and  $\omega_{1.05} = 0.05 \text{ fs}^{-1}$ , i.e. the change is about 8%.

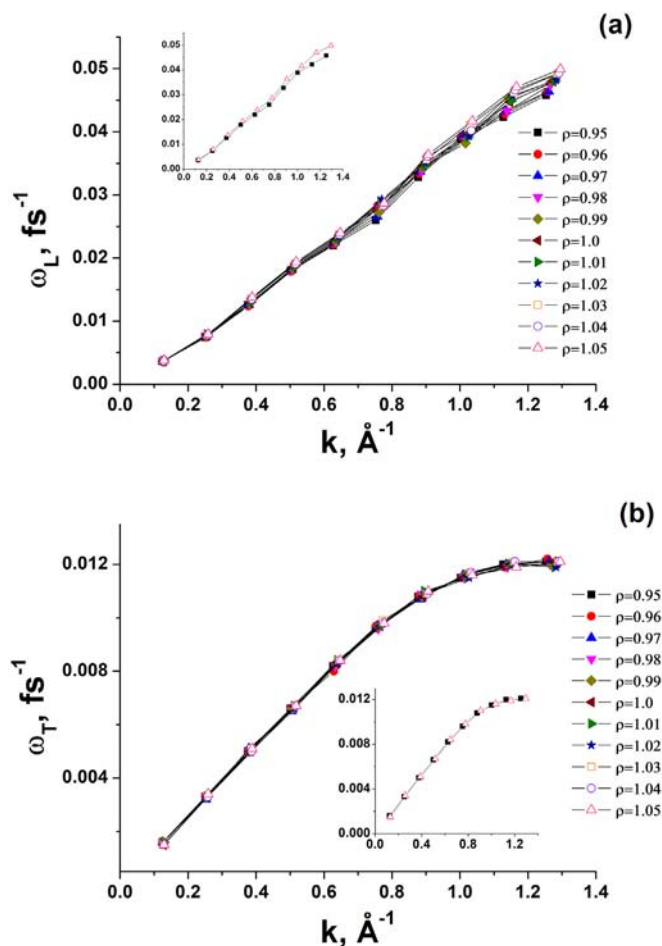
In the case of transverse excitations all curves almost coincide irrespective of the density.



**Fig. 3.** (a) Positive sound dispersion of water along isochore  $\rho = 1.01 \text{ g/cm}^3$ . (b) The same at fixed wave vector  $k = 1.28 \text{ \AA}^{-1}$ .

The results for both longitudinal and transverse excitations are in contrast to the behavior of simple liquids. In our previous works we studied the dispersion curves in the Lennard-Jones [45] and soft sphere systems [46]. It was shown that both longitudinal and transverse branches strongly depended on the density.

The behavior of water is remarkably more complex than that of simple liquid. Among the most common interpretations of water behavior is the existence of the second critical point in the deeply supercooled region [47]. However, many aspects of the behavior of water can be studied using some simplified systems which allow clear interpretation of the results. One of such systems was introduced and widely studied in our previous works [48–52]. It was shown that the system demonstrated a complex phase diagram and water-like anomalies, for instance, density and diffusion ones. The system is characterized by multiscale potential which induces its quasibinary behavior that can be clearly seen from evolution of the radial distribution functions along isochores or isotherms [48]. Such behavior may be interpreted as a smooth structural crossover between structures with different length scales of the potential. Such a crossover is responsible for many anomalous properties like density, diffusion and structural anomalies or a high value of heat capacity [53,54]. In the context of the present work the smooth structural crossover makes the system effectively softer under isochoric heating, which reduces the frequencies. Whereas frequencies should grow with an increase in temperature the opposite effect takes place in the anomalous region, which leads to a frequency decrease. Similar behavior should be expected in other anomalous liquids, for instance, liquid silicon [55] whose qualitative behavior is very close to that of the model system from [48].



**Fig. 4.** The dispersion curves of the SPC/E water model along isotherm  $T = 240$  K. Panel (a) shows the dispersion of longitudinal excitations, while panel (b) that of transverse excitations. The insets on both panels enlarge the lowest and the highest density ( $\rho = 0.95$  and  $1.05$  g/cm<sup>3</sup>). The numbers on the plots denote density in g/cm<sup>3</sup>.

#### 4. Conclusions

We studied the dependence of the excitation frequency of water along the isochore and the isotherm crossing the density anomaly region. We showed that the frequency of longitudinal excitations demonstrated anomalous dependence on temperature along the isochore. At the same time the difference in behavior of both longitudinal and transverse excitation frequencies at different densities along the isotherm was very modest or even negligible, which can also be considered as anomalous compared with the behavior of these quantities in a simple liquid.

This work has been carried out using computing resources of the federal collective usage center Complex for Simulation and Data Processing for Mega-science Facilities at NRC "Kurchatov Institute", <http://ckp.nrcki.ru/>, and supercomputers at Joint Supercomputer Center of the Russian Academy of Sciences (JSCC RAS). The work was supported by the Russian Science Foundation (Grants No 19-12-00111).

#### References

- [1] N.W. Ashcroft, N.D. Mermin, *Solid State Physics*, Saunders Colledge Publishing, 1976.
- [2] C. Kittel, *Introduction to Solid State Physics*, John Wiley, 1953.
- [3] J.P. Boon, S. Yip, *Molecular Hydrodynamics*, McGraw-Hill International Book Company, New York, 1980.
- [4] T. Scopigno, G. Ruocco, F. Sette, *Rev. Mod. Phys.* 77 (2005) 881.
- [5] K. Trachenko, V.V. Brazhkin, *Rep. Prog. Phys.* 79 (2016), 016502.
- [6] D. Bolmatov, V.V. Brazhkin, K. Trachenko, *Sci. Rep.* 2 (2012) 421–427.
- [7] S. Hosokawa, M. Inui, Y. Kajihara, S. Tsutsui, A.Q.R. Baron, *J. Phys. Condens. Matter* 27 (2015), 194104.
- [8] S. Hosokawa, et al., *Eur. Phys. J. Special Topics* 196 (2011) 85–93.
- [9] A.V. Mokshin, R.M. Khusnutdinov, A.G. Novikov, N.M. Blagoveshchenskii, A.V. Puchkov, *J. Exp. Theor. Phys.* 121 (2015) 828–843.
- [10] S. Hosokawa, M. Inui, K. Matsuda, D. Ishikawa, A.Q.R. Baron, *J. Phys. Conf. Ser.* 98 (2008), 022004.
- [11] S. Hosokawa, W.-C. Pilgrim, F. Demmel, *J. Non-Cryst. Solids* 353 (2007) 3122–3128.
- [12] S. Hosokawa, M. Inui, K. Matsuda, D. Ishikawa, A.Q.R. Baron, *Phys. Rev. B* 77 (2008), 174203.
- [13] S. Hosokawa, et al., *J. Phys. Condens. Matter* 25 (2013), 112101.
- [14] F. Demmel, S. Hosokawa, M. Lorenzen, W.-C. Pilgrim, *Phys. Rev. B* 69 (2004), 012203.
- [15] F. Demmel, S. Hosokawa, W.-C. Pilgrim, *J. Alloys Compd.* 452 (2008) 143–148.
- [16] S. Hosokawa, F. Demmel, W.-Ch. Pilgrim, M. Inui, S. Tsutsui, A.Q.R. Baron, *Electrochemistry* 77 (2009) 608.
- [17] G. Monaco, A. Cunsolo, G. Ruocco, F. Sette, *Phys. Rev. E* 60 (1999) 5505.
- [18] T. Yamaguchi, K. Yoshida, N. Yamamoto, S. Hosokawa, M. Inui, A.Q.R. Baron, S. Tsutsui, *J. Phys. Chem. Solids* 66 (2005) 2246–2249.
- [19] R.M. Yulmetyev, A.V. Mokshin, P. Hanggi, V.Y. Shurygin, *JETP Lett.* 76 (2002) 147–150.
- [20] R.M. Yulmetyev, A.V. Mokshin, P. Hanggi, V.Yu. Shurygin, *JETP Lett.* 76 (2002) 147–151.
- [21] A.V. Mokshin, R.M. Yulmetyev, P. Hanggi, *J. Chem. Phys.* 121 (2004) 7341–7346.
- [22] A.V. Mokshin, R.M. Yulmetyev, R.M. Khusnutdinov, P. Hanggi, *J. Exp. Theor. Phys.* 103 (2006) 841–849.
- [23] A.V. Mokshin, R.M. Yulmetyev, R.M. Khusnutdinov, P. Hanggi, *J. Phys. Condens. Matter* 19 (2007) 046209(1)–046209(16).
- [24] A.V. Mokshin, B.N. Galimzyanov, *J. Phys. Condens. Matter* 30 (2018), 085102.
- [25] D. Levesque, L. Verlet, J. K urkijarvi, *Phys. Rev. A* 7 (1973) 1690.
- [26] <http://www1.lsbu.ac.uk/water/wateranomalies.html>.
- [27] C. Lind, *Materials* 5 (2012) 1125–1154.
- [28] Yu. D. Fomin, E. N. Tsiok, V. N. Ryzhov, V. V. Brazhkin, arXiv:1812.09695 (2018).
- [29] H.J.C. Berendsen, J.R. Grigera, T.P. Straatsma, *J. Phys. Chem.* 91 (1987) 6269–6271.
- [30] C. Vega, J.L.F. Abascal, M.M. Conde, J.L. Aragones, *Faraday Discuss.* 141 (2009) 251–276.
- [31] C. Vega, J.L.F. Abascal, *Phys. Chem. Chem. Phys.* 13 (2011) 19663–19688.
- [32] J.P. Hansen, I.R. McDonald, *Theory of Simple Liquids*, Elsevier, 2013.
- [33] D.C. Rapaport, *The Art of Molecular Dynamics Simulation*, Cambridge University Press, 1995.
- [34] M. Canales, L.E. Gonzalez, J.A. Padro, *Phys. Rev. E* 50 (1994) 3656.
- [35] K. Hoshino, S. Tanaka, F. Shimojo, *J. Non-Cryst. Solids* 353 (2007) 3389–3393.
- [36] M. Sampoli, U. Bafle, E. Guarini, F. Barocchi, *Phys. Rev. Lett.* 88 (2002), 085502.
- [37] C. Yang, M.T. Dove, V.V. Brazhkin, K. Trachenko, *Phys. Rev. Lett.* 118 (2017), 215502.
- [38] <http://lammps.sandia.gov/>.
- [39] V.V. Brazhkin, et al., *Phys. Rev. E* 85 (2012), 031203.
- [40] V.V. Brazhkin, et al., *Phys. Rev. Lett.* 111 (2013), 145901.
- [41] V.V. Brazhkin, et al., *Physics-Uspexhi* 55 (2012) 1061.
- [42] Yu.D. Fomin, V.N. Ryzhov, E.N. Tsiok, V.V. Brazhkin, *Sci. Rep.* 5 (2015), 14234.
- [43] C. Yang, V.V. Brazhkin, M.T. Dove, K. Trachenko, *Phys. Rev. E* 91 (2015), 012112.
- [44] Yu.D. Fomin, V.N. Ryzhov, E.N. Tsiok, V.V. Brazhkin, K. Trachenko, *J. Phys. Condens. Matter* 28 (2016), 43LT01.
- [45] V.V. Brazhkin, Yu.D. Fomin, V.N. Ryzhov, E.N. Tsiok, K. Trachenko, *Phys. A* 509 (2018) 690–702.
- [46] P.H. Poole, F. Sciortino, U. Essmann, H. Eugene Stanley, *Nature* 360 (1992) 324–328.
- [47] Yu.D. Fomin, N.V. Gribova, V.N. Ryzhov, S.M. Stishov, Daan Frenkel, *J. Chem. Phys.* 129 (2008), 064512.
- [48] Yu.D. Fomin, E.N. Tsiok, V.N. Ryzhov, *J. Chem. Phys.* 135 (2011) 234502.
- [49] Yu.D. Fomin, V.N. Ryzhov, *Phys. Lett. A* 375 (2011) 2181–2184.
- [50] Yu.D. Fomin, E.N. Tsiok, V.N. Ryzhov, *Eur. Phys. J. Special Topics* 216 (2013) 165–173.
- [51] Yu.D. Fomin, E.N. Tsiok, V.N. Ryzhov, *J. Chem. Phys.* 135 (2011) 124512.
- [52] Yu.D. Fomin, *J. Phys. Chem. Liq.* 57 (2019) 67–74.
- [53] Yu.D. Fomin, *Mol. Phys.* (2018) <https://doi.org/10.1080/00268976.2018.1552801>.
- [54] V.V. Vasishth, J. Mathew, Sh. Sengupta, S. Sastry, *J. Chem. Phys.* 141 (2014), 124501.