Collective dynamics in liquids: today and tomorrow

The first phenomenological approaches to the study of relaxation dynamics in fluids can be traced back to the middle of the 19th century [1,2]. In the 1930s Landau and Placzek [3] demonstrated the first success of the macroscopic treatment of liquid dynamics. However, only in the middle of the 20th century it became clear that a deeper understanding of the physical properties of liquids could have been reached only through a microscopic description of the atomic dynamics. This was achieved through statistical mechanics which provided the necessary tools (time correlation functions, master equations, kinetic approaches, etc). The mathematical difficulties related to the treatment of real liquids brought the importance of numerical approaches to the general attention. About 50 years ago the first molecular dynamics (MD) simulations [4,5] opened up entirely new prospects for the exploration of collective dynamics in liquids on nanoscales. The well-known result by Van Hove [6] regarding the relation between the scattered intensity and time-dependent density-density correlations provided a bridge between the scattering experiments and pure theory of liquid dynamics based on linearized hydrodynamics, while the subsequent MD simulations became the main tool of numerical studies of collective processes in disordered systems on microscopic scales. The possibility to calculate different time correlation functions from MD simulations caused an extremely large number of theoretical studies on generalization of hydrodynamic theory on molecular range. The molecular hydrodynamics [7] based on Mori-Zwanzig projection formalism [8,9] still remains the main basis for the theory of collective processes in liquids.

From the experimental side the first spectral measurements of collective excitations by light scattering are dated back to the twenties of the last century. The 1950s saw major experimental efforts related to the development of Inelastic Neutron Scattering facilities which constitutes a privileged probe to access the microscopic dynamics in condensed matter and, in particular, in the liquid state. A further experimental breakthrough, however, happened in the last ten years when X-rays came up by the side of neutrons to study the collective dynamics in a similar frequency and wavelength region. The intriguing theoretical possibility of performing Inelastic X-ray Scattering became a reality due to the advent of the third generation sources, disclosing the previously unaccessible tasks in the physics of disordered systems. The most recent piece added to the energy momentum kinematic puzzle is represented by Inelastic Ultraviolet Light Scattering techniques for exploration of collective dynamics in liquids. In the years to come we are expecting to see the full coverage of the length and time scale relevant for liquids. Several large-scale facilities worldwide are developing new Inelastic Scattering setups and a synchrotron, in particular, they are investing a lot to reach energy resolutions as good as 0.1 meV, an achievement which would practically fill the gap between light and X-ray scattering. However, while the coverage of the kinematic plane is advancing with such a rapid pace, there still exists a gap between the needs of experimentalists in analysing the experimental data and the generalized theoretical models applicable to the detection of non-hydrodynamic processes in liquids. Besides, the standard computer simulations are quite frequently performed within the simplified models of effective interactions, that does not permit a direct analysis of experimental data. The development of *ab initio* molecular dynamics [10,11] opens up new challenges in the precise analysis of experimental data as well as the estimation of the effect of electron density fluctuations on the atomic dynamics in metallic, ionic liquids and systems with covalent bonds.

During the last two decades, many theoretical and experimental groups switched their studies to the search for manifestation of non-hydrodynamic processes in liquids, i.e., the collective processes that cannot be predicted using ordinary hydrodynamics. The examples of such non-hydrodynamic propagating excitations are the shear waves, the well-known “fast sound” [12] in binary liquids with disparate masses, or charge waves in ionic melts [13], while the most obvious non-hydrodynamic relaxation process is structural relaxation. There is still no general agreement on the dispersion law and damping of non-hydrodynamic processes as well as their effect on the propagating sound

excitations on different time and length scales. The situation at extreme thermodynamic conditions relevant to the earth interior and geophysical science is even less clear.

Within this context, the main idea of this Special issue was to bring together experimental, theoretical and simulation groups in order to present the recent developments in experimental techniques, new possibilities of experimental studies, different methods of analysing the experimental data, recently elaborated theoretical approaches and modern simulation techniques - all focused on collective processes in liquids. Fifteen research groups from Italy, Germany, France, Japan, Spain, Great Britain, United States, Korea and Ukraine report in this volume the current studies and small reviews of their experimental/theoretical methodology.

The review of neutron scattering technique, and of the methods of analysing the scattering intensities is presented in the paper by J.-B.Suck, while novel possibilities of a new small-angle time-of-flight neutron spectrometer (BRISP) in the studies of collective dynamics in liquids are reported by German-Italian group (A.Orecchini, W.-C.Pilgrim, C.Petrillo, J.-B.Suck, F.Sacchetti).

The problem of "fast sound" excitations in disparate-mass two-component liquids is a long-standing issue. In their paper G.Ruocco and F.Sette review the experimental and theoretical studies of the "fast sound" in liquid water, emphasizing the ground breaking contribution of the pioneering Inelastic X-ray Scattering experiments performed at the ESRF.

The recent study of collective dynamics in liquid and supercooled water by the Inelastic Ultraviolet Scattering is reported in the paper by C.Masciovecchio, F.Bencivenga and A.Gessini. The main focus is on the role of structural relaxation in water and its dependence on temperature and pressure.

D.L.Price, L.Hennet, I.Pozdnyakova and M.-L.Saboungi report their experimental studies of collective excitations in liquids at high temperatures using levitation technique and Inelastic X-ray Scattering. Results are presented for liquid Al_2O_3 and two MgO-containing oxides, as well as for liquid silicon and titanium.

Two papers from the Japanese community highlight the state-of-the-art scenario of collective dynamics in liquids at extreme conditions, based on the high-temperature high-pressure setup originally introduced by K.Tamura, that has been then developed and successfully exploited for Inelastic X-ray Scattering experiments mostly performed at the SPring8 facility.

In their paper, F.J.Bermejo, F.Fernandez-Alonso and C.Cabrillo summarize their neutron scattering and muon spectroscopy studies in monoatomic and molecular liquids. The main focus is made on wavenumber dependence of characteristic times associated with different relaxation processes: structural relaxation, self-diffusion, molecular reorientation, dielectric relaxation, etc.

A review of the memory function (MF) formalism at different degrees of approximation is presented in the paper by U.Bafile, F.Barocchi, E.Guarini. Theoretical models are applied to the analysis of spectral functions in rare fluids, methane and rare-gas mixtures.

A very interesting treatment of collective dynamics in liquid metals based on a model of the interacting two-component ion-electron plasma is reported in the paper by L.Bove, C.Petrillo and F.Sacchetti. A generalization of the Bohm-Staver model on the case of finite-size ion cores and effective electron-ion interaction is proposed. The results are shown for a large number of liquid metals covering a wide range of electron densities.

A mode-coupling theory of collective processes in liquids is developed in the study by W.Schirmacher and H.Sinn. A closed system of equations with non-local coupling is obtained and numerically solved for a hard-sphere-like model. Special attention is paid to relaxation processes in liquid dynamics. It is demonstrated that the memory function is represented as a sum of two exponentials, one of which is identified as a strongly density dependent one and responsible for α-relaxation, while the second, short-time relaxation process, is independent of density.

Ukrainian group (T.Bryk and I.Mryglod) is focused on the development of the theoretical method of analysis of time correlation functions known as the approach of Generalized Collective Modes (GCM). The main difference of the GCM with the regular MF approach consist in the explicit treatment of different types of dynamical variables for the construction of matrix form of generalized Langevin equation, which is solved in terms of dynamical eigenmodes. Such an approach avoids *a priori* the modeling of the explicit time dependence of the highest-order memory function

and leads to very transparent results by associating dynamical eigenmodes with specific types of dynamical variables or their linear combinations. In the actual contribution a new perturbation approach within the GCM scheme is reported, which appeared to be very useful in the analytical study of long-wavelength collective modes, and is very promising for analytical studies of collective dynamics in binary and many-component liquids.

A new approach in ab initio simulations of liquids, based on orbital-free form of electron density functional, and its application to the collective dynamics of liquid binary alloys is reviewed in the paper by D.J.Gonzalez and L.E.Gonzalez. An essential advantage of the orbital-free ab initio MD over the regular ab initio MD techniques such as Car-Parrinello dynamics or direct energy minimization of electronic degrees of freedom for each instantaneous ionic configuration (Born-Oppenheimer surface) is that there is no need in self-consistent solving the Kohn-Sham equations for a large number of valence wave functions (orbitals), which at each time step should be mutually orthogonal. This results in a large number of atoms which can be simulated with orbital-free ab initio MD -up to several thousands, which is the same as in classical MD simulations. These possibilities of orbital-free ab initio MD are demonstrated in the study of dispersion curves of collective excitations in metallic binary alloys with the mass ratio of the components changing in a wide range, which brings a new insight on the formation of high-frequency propagating excitations.

New sophisticated models of interaction potentials are especially important for the simulation studies of ionic systems, where polarization effects play an important role. A molecular dynamics study of collective dynamics in the ionic melt Al_2O_3 based on a new MD technique is reported by S.Jahn and P.A.Madden. It is proposed to explicitly take into account the changes in the shape of ions due to polarization effects via estimation of dipolar and quadrupolar shape distortions for each instantaneous ionic configuration using a conjugate gradient minimization technique. Dispersion and damping of acoustic excitations, as well as frequency-dependent viscosity of the alumina melt are reported.

An important theoretical problem of the dynamics of solute particles in molecular solvents is in focus of Korean-Japanese group (B.Kim, S.-H.Chong,R.Ishizuka, F.Hirata). A system of equations of motion for dynamical variables describing solute particles and solvent was obtained, which results in a static and dynamic coupling between the solute and the solvent. The importance of the results is in the form of a dynamical equation for a solute, which is similar to Langevin equation, but with microscopic description of each term.

All the contributions presented in this volume represent the state-of-the-art experimental, theoretical or simulation techniques used for the exploration of collective dynamics in various liquid systems. One can hope that the Special issue will help in exchanging the information on the recent progress in experimental, numerical and theoretical approaches. A careful comprehensive analysis of the reported contributions can also provide the basis for new studies of collective dynamics in liquids and set the playground for the next generation of researchers in the field. Topics which should deserve special attention include:

- the development of reliable methodology of analysis of experimental dynamical structure factors based on appropriate theoretical models, which would close the gap between theory and experiment;

- the search for a possible manifestation of non-acoustic modes in the dynamical structure factors (the emergence of non-hydrodynamic overdamped high-frequency excitations due to association in liquids, or transverse-like excitation) and their theoretical explanation;

- understanding the tendency in dispersion laws of collective excitations in strongly asymmetric (in size, mass, composition, charge) binary and many-component liquids, which would make a bridge to the microscopic theory of hydrodynamic interaction mediated by the subsystem of light particles;

- the development of new approaches in order to explicitly account for the role of conduction electrons in dynamics of liquid metallic systems;

- understanding the features in the behavior of collective excitations in liquid systems at extreme thermodynamic conditions;

- the development of a theory and precise experimental techniques for the exploration of collective dynamics at liquid surfaces and interfaces.

Such a list cannot be considered as a complete one. The advance in experiment, theory and simulations always poses new questions for researchers. It would be nice, however, to see the relevant efforts in the directions mentioned above. We are grateful to all research groups that contributed to this Special issue, and express our belief that the joint efforts of experimental and theoretical groups will results in new exciting results in the field of collective dynamics in liquids.

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guest editors
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