

THE EARLY YEARS OF CONDENSED MATTER THEORY IN MESSINA

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Abstract

Topics of condensed matter theory on which research was started in Messina in the period 1969-74 are briefly reviewed. Developments of lasting value concerning structure and dynamics of molten salts, solutions of ions in water, and electron gas theory are all mentioned and illustrated.

1 - Foreword

It is with great pleasure that I have welcomed the invitation to contribute to this Festschrift Volume honouring my friend Enzo Grasso on his seventieth birthday. I am already past this threshold and know that, while in advance one is seldom conscious that it will come, it is gratifying when one reaches it to think back to the experiences that one has had in the past. I have thus felt it appropriate to reminisce on this occasion about those five years during which Enzo and I were together in the old building of the Istituto di Fisica in the central court of the University in Messina. I am confident that this will please him more than if I were to contribute some technical account of my current research interests. And what could be better for both of us than to think back to those years when so many of the present members of the physics community in Messina were starting off on their careers ?

In the retrospect the years that I spent in Messina have indeed been one of the most gratifying and exciting periods in my life. I was returning in 1969 to Italy, that I had left as a young post-doc to work for many years in research laboratories abroad. It was my first official employment in a position of responsibility with an academic institution. A number of students and of newly graduated young people joined the Istituto in those years and were providing the

new blood for the growth of research in condensed matter physics inside it. This growth invested the pre-existing experimental group led by Enzo in the general area of semiconducting materials, as well as the newly created experimental group led by Franco Wanderlingh in the areas of soft condensed matter and disordered materials and the theoretical group that started condensing around me.

I shall not attempt to give a full review of how these various activities developed during those five years and how they continued growing up to their present status inside the Physics Departments and the University. Intermediate "progress reports" have been published in 1989 by Grasso and Neri (1) concerning the electronic properties of hydrogenated amorphous silicon, and by Carini and Maisano (2) on relaxation processes in liquids and glasses. I shall rather try to present some recollections of the theoretical lines of research that were started in those years and shall simply mention some of their outgrowths that took place during my later peregrinations through other academic institutions. A short review of their sequel in Messina has been given in 1989 by Caccamo (3), with specific reference to theoretical studies of molten salts and concentrated electrolytic solutions.

2 - Molten salts: structure and dynamics

In spite of the relevance of molten salts in inorganic chemistry and of their numerous technical applications, the characterization of their structure by physical methods was in 1969 still in its infancy. An X-ray diffraction experiment yields only the total pattern of a liquid compound and is usually almost blind to chemical short-range order. This type of order is instead the main structural trait of a system such as molten sodium chloride, where the Coulomb interactions manifest themselves in producing a first-neighbour shell of chlorine ions around each sodium ion and *vice versa*. The local structure of the liquid thus preserves the main features of the crystalline state and the liquid-state cohesion is still due to electronic charge transfer between the component elements, although the first-neighbour coordination number in the melt is somewhat reduced relative to that holding in the solid state.

An early study of molten lithium chloride by M. A. Bredig and coworkers (1960) had

used a combination of X-ray and neutron diffraction to partially unravel the underlying correlations of the three types of ion pairs. As the end of the 1960's was approaching it was expected that full resolution would soon be achieved experimentally by means of a technique of neutron scattering from liquid samples of different isotopic compositions, which had been previously developed for liquid metal alloys. This method of neutron diffraction from isotopically enriched samples has taken advantage of the fact that the scattering intensities of the ^{35}Cl and ^{37}Cl isotopes of chlorine differ by a factor of about five in order to obtain detailed structural data on molten chlorides, first with the work of D. I. Page and K. Mika (1971) on molten copper chloride and then with the systematic studies carried out in England by J. E. Enderby and E. W. J. Mitchell and in France by J. Dupuy and P. Chieux on monovalent and divalent metal chlorides. At the same time classical computer simulation studies were being started by L. V. Woodcock and K. Singer (1971), using the empirical interionic pair potentials that Fausto Fumi and I had developed back in 1964 for alkali halide crystals (without foreseeing, I must say, that our results would become most useful in the future as models for their melts). With these perspectives there was for us in Messina a clear opportunity to do relevant theoretical work in an as yet underdeveloped area of growing experimental interest - and what better opportunity could be found for a newly formed group of theorists working in a situation of relative isolation, such as we were at that time ?

It was therefore very timely that we should in those years engage in theoretical work on the static and dynamic structure of molten alkali halides. With Tina Abramo and Michele Parrinello we started out by setting up a parallelism between molten salts and binary alloys (4), which developed into a precise definition of the state of chemical short-range order in an ionic melt in terms of correlations between the ionic charges. Our work provided the first compelling proof of the usefulness of the concept of correlations between composition fluctuations, that had been introduced for liquid metal alloys by A. B. Bhatia and D. E. Thornton (1970): whereas composition fluctuations were at the time viewed by other workers as merely leading to "incoherent scattering", our viewpoint that these correlations are of the essence in a molten salt was to become generally accepted in describing short-range order in these materials.

A crucial aspect of the so-called Fumi-Tosi interionic potential is the role played by the

ionic radii in determining the effective short-range interactions between the various ion pairs. Fausto and I had been able to attribute a precise meaning to parameters entering the ionic interactions in terms of the relative sizes of the cation and the anion in each alkali halide crystal and to relate this quantity to the effect of the crystal field on the outer electron shells, that could be measured in diffraction experiments of very high accuracy. The next important development in our studies of molten salt structure involved also Carlo Caccamo and Giovanni Pizzimenti (5, 6) and aimed to show, with main attention to providing useful guidance for diffraction experiments, how the ionic sizes should be expected to enter the structure of the melt in determining the first-neighbour coordination number and the shapes of the partial diffraction patterns from the three types of ion pairs. We were able in this work to provide an interpretation of the experimental data reported by Page and Mika for molten copper chloride, in terms of a basically ionic liquid structure in which some residual covalency and "crystal field" effects are emerging through an unexpectedly small value of the radius of the copper ion.

At the same time we were pioneering the theory of the dynamical properties of alkali halide melts. With Tina Abramo and Michele Parrinello we made predictions on the dynamic structure factors that enter the neutron inelastic scattering cross-section (7). The thesis work of Paolo Giaquinta gave the theory of the hydrodynamic behaviour of molten salts (8), with results that were verified during a School on Statistical Mechanics in Les Houches against those obtained some time later by the group of J.-P. Hansen in Paris. Paolo then extended his studies of charge and mass transport in molten salts into the microscopic regime, giving the basic theory of these phenomena and providing the interpretation of a number of classical computer simulation runs and of some real experiments (9 -12). Four main results were achieved in his work: (i) mass transport is partly taking place through the correlated motions of electrically neutral groups of ions, superposed onto the single-ion transport mechanisms which are revealed by ionic conduction; (ii) the dielectric formalism allows one to directly relate the spectra obtained from separate simulation studies of ionic currents and of charge density fluctuations; (iii) the spectrum of charge density fluctuations at long wavelengths can be deduced from the measured reflectivity spectrum and consists of one hydrodynamic component and one optic-mode component; and (iv) the dispersion and broadening of the polaritonic

spectrum can be exhibited from the reflectivity spectrum. Some other workers maintained at that time that the spectrum of charge fluctuations would indeed contain two contributions, but they should both be either hydrodynamic modes or optic-like modes; or alternatively that an optic-like mode could not exist in a molten salt. The analysis of the measured reflectivity spectrum of molten lithium fluoride that Paolo produced in support of our theory got rid of these misconceptions.

These activities on molten salts culminated in a joint review article with Michele Parrinello (13). As will be seen from the list of references given so far, these theoretical activities were continued in collaboration with the young theorists in Messina after my transfer to the University of Rome and then to Trieste. Three further main lines of research with later coworkers in this area may be mentioned. These concerned the state of a solvated electron in a molten alkali halide, first studied in his thesis by Gaetano Senatore; the theory of freezing, order-disorder transitions, and interfacial phenomena in ionic systems, which was developed in Trieste mainly together with Mauro Rovere, Pietro Ballone, and Giorgio Pastore; and the formation and stability of complex anions in molten halides of polyvalent metals, which went on for a number of years till very recently in collaboration with Zehra Akdeniz and her students in Istanbul.

3 - Electrolyte solutions

My collaborations with Paolo Giaquinta had started with the preparation of his thesis work on the hydrodynamics of molten salts, as recorded above, and continued for a number of years after I left Messina. We were mostly interacting together with Norman March in Oxford: in particular, one of our earlier collaborations concerned the interpretation of the power laws that are commonly observed in the frequency dependence of the dielectric function of disordered systems (14).

Our main work with Norman, however, was devoted to the study of the diffusion coefficients of polyvalent cations in water and to the inferences that these data could provide on the local structure of the water molecules and of the anions in the coordination shell of these

cations inside electrolytic solutions. In this connection Norman was able to enlist the help of an experimental group in Canberra, who carried out measurements of the diffusion coefficients of nickel (15), zinc (16), and cadmium (17) in aqueous solutions as functions of temperature and concentration. The observed formation of monosulphate and disulphate complexes of cadmium in concentrated solutions of cadmium sulphate motivated us to propose a novel statistical model allowing for non-additivity of the radii of the two ionic species in an ionic fluid (18). We showed that negative deviations from additivity lead to cation-anion pairing in the absence of covalent binding, while positive deviations favour demixing up to pairing of like ions.

Finally, with Paolo we published a joint review chapter, covering both molten salts and concentrated electrolytic solutions, within a series of volumes devoted by Elsevier to the chemical physics of solvation (19).

4 - The electron gas

The homogeneous gas of electrons assuredly is the most important basic model in the physics of condensed matter. It was first used by Drude in 1900 to treat the electromagnetism of plasmas and was developed by the pioneers of quantum mechanics in the early 1930's to evaluate the contribution brought by the sea of interacting conduction electrons to the cohesive properties of metals. The model was the object of renewed attention in the 1950's in connection with the experiments of electron energy loss in metals from the excitation of bulk and surface plasma modes in the sea of conduction electrons. Finally, through the development of density-functional theory in the 1960's it has become the basic reference system for most calculations of electronic structure in metallic or insulating solids and liquids, and is also often used in quantum chemistry problems concerning atomic-scale systems up to biomolecules. I may recall in this context the award of a Nobel Prize in Chemistry to Walter Kohn and the vast recognition achieved by the Car - Parinello computational method by combining the methods of molecular dynamics and of density-functional theory to simultaneously follow the evolution of the valence electrons and of the ionic cores in a parameter-free quantum mechanical approach.

During the last few years of my stay in the United States I had started working with

Kundan Singwi on the theory of the electron gas and it was a challenge in 1969 to import this highly qualified and competitive field of theoretical research into Italy through Messina. In this I was helped by Tadashi Arai, with whom I had shared an office for several years in the Materials Science and Solid State Science buildings at the Argonne National Laboratory, and by Norman March, whom I had first met at a scientific meeting on lattice defects in Tennessee. Tadashi spent one year in Messina, during which he initiated Michele Parrinello in the theory of spin-spin correlations (20) and myself in a functional-derivative formulation of electronic hopping as described by the Hubbard model in the strong-correlation regime (21). Norman spent in Messina just two weeks in 1972, but his visit marked the beginning of a lasting collaboration which is still continuing today and has produced over the years three books and some eighty research papers, in addition to a number of reviews and co-edited volumes. In those two weeks we were able to complete a paper presenting the theory of the propagation of plasmon excitations in crystal lattices (22). Later collaborations with Norman involved also Michele Parrinello (see for instance (23) and (24)) and Paolo Giaquinta, as already recorded in the context of electrolyte solutions.

In parallel with the above studies, some other young researchers in the Institute of Physics in Messina were involved in work on properties of the electron gas. Thus, Tina Abramo explored in great detail and thoroughness the relationship between quantum and classical plasmas in regard to the theory of pair correlations and dielectric screening (25). Giovanni Pizzimenti and Attilio Villari evaluated Landau's interaction parameters in the Fermi-liquid theory of the electron gas, with special focus on the many-body enhancement of the spin susceptibility and on the interpretation of experimental data for alkali metals that had newly appeared in the literature (26). Carlo Caccamo and Giovanni Pizzimenti worked out the microscopic theory of dielectric response and longitudinal spin response in an electron gas carrying an unbalance between the two spin populations (27).

The theory of the interacting electron gas still is a focal theme of interest worldwide and in particular for a number of young people that are currently working in my group in Pisa, in the deeply changed scenario that is now prevailing. A great expansion in this field of research has taken place under the impulse from the development of quantum simulation techniques,

such as those practiced by Pietro Ballone, and from the realization of semiconductor devices using man-made materials, in which the electronic carriers are constrained to move in reduced dimensionalities (*i.e.* in quantum wells, quantum wires, and quantum dots). There also are expectations that spin-resolved electronics (or "spintronics") may soon provide viable new tools in technology. It is thus fitting to record here that in Pisa we have quite recently found new usefulness for the aforementioned work of Caccamo and Pizzimenti (27) to suggest on one side a new cooling mechanism for atomic Fermi gases inside magnetic traps, and on the other to formulate new approaches to the theory of spin correlations and of spin transresistivity in two-dimensional electronic conductors.

5 - Concluding remarks

In conclusion, it is appropriate for me to acknowledge some other members of the community that were working in condensed matter theory in Messina at that time. I refer in particular to Cubiotti, Donato, and Giuliano for their work on metals and alloys; to Girlanda for his work on the optical properties of solids; and to Moscheo for his unquenchable passion for the history of physics. Let me thank them on this occasion together with the theorists that I have mentioned above and with all the experimentalists with whom we shared those exciting years.

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