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METAL-HALIDE SYSTEMS: FROM MOLECULAR CLUSTERS TO LIQUID-STATE STRUCTURE

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ABSTRACT. I present a short review of the relationship between quantum-mechanical calculations on small molecular clusters of some metal-ion halides and studies of the microscopic structure in the condensed liquid phases of these compounds. The review is dedicated to the memory of Professor Vincenzo Grasso.

1. Introduction

After the early achievement of partial resolution of short-range order in molten LiCl by Levy *et al.* (1960) through the combined use of X-ray and neutron diffraction, interest began in the early seventies of the past century to focus on obtaining full resolution both in various English groups and in Messina. A Monte Carlo study of a model ionic liquid simulating molten KCl by Woodcock and Singer (1971) at Egham College demonstrated that alternation of the two ionic species in space is largely preserved across melting, with the implication that ionic screening in the melt is oscillatory rather than monotonically decaying as in the famous Debye-Hückel theory. Complete experimental resolution of the three partial structure factors was achieved in molten CuCl by Page and Mika (1971) using the multipattern neutron diffraction method based on isotopic enrichment of the samples, and soon afterwards in molten NaCl by the group of John Enderby in Bristol (Edwards *et al.* 1975; Biggin and Enderby 1982) and in molten RbCl by Mitchell, Poncet, and Stewart (1976) in Oxford. The work in Messina instead addressed the theory of both static and dynamic structure of monovalent molten salts. Special attention was given to the connection between the static structure factors and the dielectric screening properties (Abramo, Parrinello, and Tosi 1973a; Abramo *et al.* 1976) and to a plasma-like mode of relative oscillation of the two ionic species which is supported by their relative microscopic order (Abramo, Parrinello, and Tosi 1973b; Giaquinta, Parrinello, and Tosi 1975). The final achievement of the theory of liquid structure and thermodynamics for a binary salt of monovalent ions at freezing was based on a hypernetted chain approach modified to impose thermodynamic self-consistency (Ballone, Pastore, and Tosi 1984). This approach yields excellent agreement with the results from computer simulations and good agreement with experiments (for a review see Rovere and Tosi 1986). Further extensions to the liquid halides of polyvalent metals and to solutions of metals in molten salts soon followed (for a review on trivalent metal halides see Tosi, Price, and Saboungi 1993).

The exploration of the structure and the physical properties of molten salts and disordered ionic solids by theoretical and computer simulation methods has largely been based on phenomenological ionic models stemming from the early work of Born and Mayer (1932) on alkali halide crystals. The "Born model" invokes the classical Coulomb interactions between the ions and their van der Waals attractions as balancing the quantum overlap repulsions of closed electronic shells in the equilibrium of the crystal (for a review see Tosi 1964). The strength of the repulsions is exponentially weighted by ionic radii that are related to the measurable sizes of the ionic cores (Fumi and Tosi 1964; Tosi and Fumi 1964). Rittner (1951) recognized the need to account for induced electronic dipoles in molecular and disordered states of these compounds: for instance, the polarization of the outer electron shell of the chlorine ion in the NaCl molecule reduces its measured dipole moment to about one-half of its rigid-ion value as determined from unitary charges located at the bond-length distance. Major effects of electronic polarization also arise in crystals in determining the energetics of point defects that are responsible for charge and mass transport (Mott and Littleton 1938) as well as the frequencies of lattice vibrations (Born and Huang 1954). In studying phonons in ionic and semiconducting crystals the so-called shell model has evolved (for a review see Cochran 1971). This model, which regards each polarizable ion as having an outer shell of valence electrons coupled to a rigid inner core and thus allows for electronic counter-dipoles driven by the overlap repulsions, was later developed into a non-linear "deformation-dipole model" in dealing with the alkali halide molecular monomers, thus achieving a unified picture which spans from crystalline to molecular states (Tosi and Doyama 1967). The deformation-dipole model has received a basic quantum-mechanical justification in a tight-binding viewpoint from a double expansion of the Hamiltonian into electrical multipoles and overlaps (Brumer and Karplus 1973).

In this short review I mainly dwell on the relationship between basic quantum-mechanical studies of small molecular clusters of metallic and halogen ions and the development of model interactions for the theory and the computer simulations of the condensed disordered phases of ionic compounds. Even at a time when *ab initio* molecular dynamics techniques are starting to be used in dealing with complex ionic liquids (East and Hafner 2007; Koura, Ohmura, and Shimojo 2013), the recourse to accurate force-law models remains useful since it allows vast explorations of the pressure-temperature plane with a relatively moderate numerical effort and the identification of the relevant parameters and physical mechanisms that are the main cause for the observed behaviours.

In brief, the outline of the review is as follows. Starting with the NaCl monomer and with the neutral and ionized Na_2Cl and $(NaCl)_2$ species in Section 2, I proceed to Zn, Cd and Hg halide systems in Section 3, the main focus here being on small clusters which appear to be relevant for dense gaseous states on the transition to the liquid state along supercritical paths. Some comments and outlooks conclude the review in Section 4.

2. Sodium chloride microclusters: fundamentals and model

Much of the fundamental interest in the alkali halide monomers derives from the fact that the two lowest adiabatic potential energy curves have the same $^1\Sigma^+$ symmetry and display an avoided crossing where an interchange of ionic and atomic bonding occurs (Jordan 1979). A good estimate of the location of the crossing $R_X \cong 0.945\,\mathrm{nm}$ in the NaCl molecule is obtained by setting $e^2/R_X = I - A$, where I is the ionization potential of the alkali atom and A the electron affinity of the halogen atom: it is therefore safe to regard the molecular ground state to be dominantly ionic near the equilibrium bond length $R_0 = 0.2361\,\mathrm{nm}$. This implies that the Hartree-Fock method already yields a fairly accurate account of the electronic ground state in the region of the bond, as was shown from configuration-interaction calculations carried out by Andreoni, Galli, and Tosi (n.d.) in a pseudopotential scheme. In this region the atomic state lies at much higher energy and is strongly repulsive towards dissociation.

At the equilibrium internuclear distance the configuration-interaction calculations yield a Mulliken-population shift in the electronic charge of $0.85e$ from Na to Cl, the electron density being polarized in the opposite direction, and show that the charge shift rapidly rises to $0.99e$ as the internuclear distance R increases. The calculated dipole moment of the molecule can be written as $\mu(R) = eR - \mu_e(R)$, where $\mu_e(R)$ is the "electronic dipole moment" due to deformations of the closed-shell configuration of an assumed Cl^- component of the molecule not far from the equilibrium bond length. One obtains in this way an effective polarizability $\alpha_{\mathrm{Cl}}(R)$ of the chlorine negative ion, which equals $3\mathring{\mathrm{A}}^3$ for $R = 3\mathring{\mathrm{A}}$, in good agreement with the value obtained from an analysis of the measured refractive index of alkali halide crystals (Tessman, Kahn, and Shockley 1953). It is also found that the effective polarizability function rapidly decreases with the internuclear distance below R_0. This behaviour provides direct evidence in favour of the deformation-dipole model, which embodies quenching of the deformability of the halogen ion with increasing interionic overlap as the bond length is decreased.

The deformation-dipole model yields the following expression for the potential energy $U(R, m_+, m_-)$ of an alkali halide monomer like NaCl, as a function of the internuclear distance R and of the electronic dipole moments carried by the two ions (Tosi and Doyama 1967):

$$U = -\frac{e^2}{R} - \frac{e(m_+ + m_-)}{R^2} - \frac{2m_+m_-}{R^3} + \frac{m_+^2}{2\alpha_+} + \frac{m_-^2}{2\alpha_-} + m_-B(R) + \phi(r) \qquad (1)$$

Here, $\alpha_\pm$ are the electrical polarizabilities of the two ions, $\phi(R)$ is their short-range interaction energy (including both overlap repulsions and van der Waals attractions), and the term $m_-B(R)$ allows for the overlap deformation dipole located on the negative ion. The dipole moment carried by the positive ion is in fact negligible in NaCl, so that $m_+ \approx 0$ and

$$m_-(R) \approx \alpha_- \left[\frac{e}{R^2} - B(R)\right] \qquad (2)$$

and

$$U(R) \approx -\frac{e^2}{R} - \left(\frac{e}{2R^2}\right) m_-(R) + \frac{1}{2} m_-(R)B(R) + \phi(R) \qquad (3)$$

upon minimization with respect to m_-. In the same limit the Rittner model is recovered upon setting $B(R) = 0$ and acquires quantitative value only through fits to measured molecular properties. One may instead take B(R) as proportional to the exponential-like repulsive part of $\phi(R)$, through a factor fixed by the quantity $(1 - (e^*/e))$ where e^* is the so-called Szigeti charge (Born and Huang 1954) as obtained from the static dielectric constant of the crystal.

TABLE 1. Properties of the NaCl molecular monomer from the deformation dipole model with parameters taken from solid-state data (DDM), from basic configuration-interaction calculations (CI) and from experiment (EXP): equilibrium bond length R_0, total dipole moment m, dissociation energy D into separated ions, and vibrational frequency ω [from Karaman, Akdeniz, and Tosi (2006)].

	DDM	CI	EXP
R_0 (Å)	2.383	2.382	2.361
m (debye)	9.58	10	9.00
D (eV)	5.71	5.43	5.75
ω (cm^{-1})	402	378	364.6

The values of e^*/e are on the range $0.7-0.9$ for alkali halide crystals, and in particular $e^* = 0.74e$ in NaCl. It is then clear from Eq. (2) that electronic deformation from overlap cuts down the electrostatically induced dipole on the halogen in an exponential manner as the internuclear distance is compressed below its equilibrium value. Such a depression is supported by the basic quantum calculations, as previously stressed.

The potential energy curve of the ionic state of the NaCl monomer as calculated in the deformation dipole model, using for its parameters (polarizabilities and ionic radii) *values known from data on crystalline sodium chloride*, is in fully quantitative agreement with that obtained from the configuration-interaction study of Andreoni, Galli, and Tosi (n.d.). Table 1 reports comparisons of model results with the basic theory and with experimental data. The clear conclusions are (i) that the classical Coulomb law between ions carrying integer charges becomes dominant above the equilibrium bond length almost up to the avoided crossing, and (ii) that the overlap terms, including the deformation dipole term, become dominant upon compression of the bond length.

Further light comes from configuration-interaction calculations on the ionization process of the monomer (Andreoni, Galli, and Tosi n.d.). From the difference in the charge-density maps of NaCl and NaCl$^+$, it is seen that in a vertical ionization the electron which is being removed comes from the highest π orbital and is strongly localized on the chlorine. When the ionized monomer relaxes towards equilibrium, the hole left by the ionization remains localized on the chlorine: the binding in the molecular ion is weak (0.44 eV) and is due to the polarization of the chlorine *atom* in the field of the sodium ion. The minimum in the potential energy curve at 2.95 Å is very shallow, in accord with the observation of broad bands in the photoelectron spectra, and the calculated potential for adiabatic ionization is 8.75 eV, to be compared with (8.93 ± 0.1) eV from the measured onset of the photoelectron bands. The Mulliken population of the outer shell of the chlorine atom is $6.94e$ at the equilibrium bond length and increases towards the dissociation-limit value $7.0e$ as the NaCl$^+$ molecular ion is stretched.

Similar messages come from the Hartree-Fock calculations of Galli, Andreoni, and Tosi (1986) on the neutral and singly ionized states of Na_2Cl and of the dimer $(NaCl)_2$, the latter being an abundant species in dense sodium chloride gases. The dimer has the shape of a rhombus, where the binding comes from an accumulation of electronic charge along the Cl$-$Cl bond at the expense of the polarization charge along the bond in the monomer. Ionization is accompanied in both molecules by symmetry breaking, leading to a linear structure for $(Na_2Cl)^+$ and to a triangular shape for $(NaCl)_2^+$. Ionization of the dimer yields a localized hole on one of the chlorines and is followed by symmetry breaking into a structure consisting of a linear $(Na_2Cl)^+$ to which a chlorine atom is weakly attached at zero temperature. Release of the chlorine atom requires an activation energy of only a few hundredths of an eV. This suggests an explanation for mass spectroscopy data on many alkali halide clusters, showing that chlorine-deficient aggregates are more often observed than stoichiometric ones.

I conclude this part of the review by remarking that models including electronic polarization of the ions have also been used in simulation studies of the structure of alkali halide melts (for a review see Rovere and Tosi 1986). Although the role of electronic polarization appears from these studies to be only minor in the liquid structure of the bulk melts in standard thermodynamic conditions, it may be more relevant in dealing with the transition from the ionic liquid to the molecular gas taking place across the liquid-gas interface, especially on the approach to the critical point.

3. Group-12 dihalides: clusters and the structure of supercritical fluid

Of material relevance to the discussion that I give in this Section on recent calculations on the molecular trimers of Zn, Cd and Hg dihalides using relativistic quantum mechanics (Özen *et al.* 2015) are the experiments of neutron diffraction at elevated temperature and pressure carried out by the Marburg group on the liquid alkali metals Rb and Cs (Winter, Pilgrim, and Hensel 1994). In these experiments the liquids are expanded towards their liquid-gas critical point and it is found that the reduction in density takes place *via* a lowering of coordination towards linear twofold-coordinated structures at essentially unchanged first-neighbour distance. We might expect this behaviour to be rather general, in view of the clear preference given by the rules of chemistry to a fairly well defined value of the first-neighbour bond length in various structures of each material and compound. We might then surmise that, along a supercritical path at increasing density that goes from the gas to the liquid, the density growth may take place through the formation of increasingly large linear clusters at approximately constant first-neighbour bond length. The halides of Zn and Cd are ideally suited for a test of this hypothesis, in view of two main facts: (i) they possess a mixed ionic-covalent bonding character, favouring the formation of clusters; and (ii) the preferred coordination is tetrahedral in all the condensed phases of Zn dihalides (Allen *et al.* 1991) and in the liquid phase of $CdCl_2$ and $CdBr_2$ (Okamoto *et al.* 2004; Shiwaku *et al.* 2005), and an average fourfold coordination already can show up for the central metal ion in the linear ground-state structure of the molecular trimer of these compounds. It should be remarked that the Hg dihalides, as a consequence of the major role played by relativistic terms to be discussed further below, do not conform to this pattern, but form ground-state clusters that are weakly bound aggregates of their molecular monomers (Kaupp and von Schnering 1994; Ruberto *et al.* 2012). The basic ground-state structure of the trimer of Zn and Cd dihalides is in Hg dihalides shifted by relativity to become a (mechanically unstable) excited state.

It is indeed found in the basic calculations of Özen *et al.* (2015, 2014) that the ground state of the Zn and Cd dihalide trimers has a linear shape, in which the average first-neighbour coordination of the central metal ion is fourfold and precisely corresponds to the tetrahedral ratio $R_{--}/R_{+-} = \sqrt{8/3} = 1.63$. Superposed on this average coordination there is a small elongation of the tetrahedron by a few percent along the molecular axis and a small squeeze by a few percent in the transverse directions, as imposed by the linear symmetry. The same result holds, within rounding-off error, for the structure of the above mentioned excited state of Hg dihalides. Of course, each of the halogen ions in these linear trimers has a strongly reduced halogen-halogen coordination, down to 3 from the bulk value 12. The hypothesis that I have exposed above is therefore fully confirmed by the fundamental (relativistic) calculations on the molecular trimers of these compounds.

Several further points deserve some discussion for these group-12 metal dihalides:

(1) Whereas the consequences of relativity are small in all cases for the small molecules of Zn and Cd dihalides, the inclusion of relativistic terms in the Hamiltonian of Hg dihalides induces a strong stiffening agains bond bending in their molecular monomers and drives their trimers to break up into a variety of configurations at closely similar energies, consisting of three distinct and almost undistorted monomers (Özen *et al.* 2015; Ruberto *et al.* 2012). One of these trimer structures can be described as a primordial strip of parallel monomers and heralds a germ of an observed crystal structure for $HgCl_2$, consisting of layers of pairs of monomer strips in a fish-bone configuration (Wyckoff 1963). The heavier Hg dihalides show higher metal-halogen coordination numbers, but again the solid can be viewed as built from molecular monomers (Wyckoff 1963). There have been no experimental studies of the structure of their liquids, which at standard pressure have only a small temperature range of stability before evaporation, but their extremely low ionic conductivity indicates that they are of molecular type, possibly with some rotational short-range order in the distribution of the small rod-like molecular monomers. We have used the results of the relativistic first-principles calculations on the small molecules of $HgCl_2$ to derive pseudoclassical interaction potentials (Ruberto, Pastore, and Tosi 2013), including three-body forces and electronic polarization terms, which could be used to explore by means of molecular dynamics the nature of the short-range and intermediate-range order in the melt and the process of ionization at high pressure and temperature.

(2) The structural behaviour of molten $CdCl_2$ and $CdBr_2$ is most remarkable, as it has been experimentally reported (Okamoto *et al.* 2004; Shiwaku *et al.* 2005) that their first-neighbour coordination number changes from four to six on freezing of the liquid at atmospheric pressure. Conversely, whereas $ZnCl_2$ and $ZnBr_2$ crystallize into polymorphs with tetrahedral coordination at standard pressure (Wyckoff 1963), X-ray diffraction experiments on molten $ZnCl_2$ under pressure (Brazhkin *et al.* 2007) have shown that a rather sharp liquid-liquid transition occurs from a tetrahedral-type network structure into an ionic-type structure. Computer simulations using an empirical force law (Ruberto, Pastore, and Tosi 2009a) have displayed a rather sharp transition in the melt under pressure, as most clearly revealed by an inversion in the magnitudes of the diffusion coefficients of the two atomic species: in essence, the Zinc ions are squeezed under pressure out of their tetrahedral-like cages while the network-like ordering of chlorines is still maintained. This is, I feel, an outstanding example of the usefulness of empirical interionic potentials. Another outstanding example, that has been reported

elsewhere in this journal (Ruberto, Pastore, and Tosi 2009b), is provided by the insulator-insulator and insulator-conductor transitions that occur under pressure in liquid $AlCl_3$.

4. Concluding remarks and future perspectives

In summary, calculational approaches based on the use of empirical interionic force laws have amply demonstrated their usefulness in the study of the structure of molten salts and of their structure-dependent properties. This also includes the discovery of liquid-liquid transitions under pressure. Although in this short review I have addressed only the prototypic alkali halide systems and the very recent studies of the group-12 dihalides, these approaches have been explored in the literature for up to the halogen compounds of pentavalent metals. It remains a challenge to look for practicable methods to model materials on the atomic scale, without having to simulate electrons explicitly (see, *e.g.*, Bartók *et al.* 2010).

Of course, the predictive accuracy of such potentials is an important aspect of this type of approach, and indeed fundamental calculations on small molecular clusters can be very helpful for enhancing its usefulness. Nevertheless, the interesting issues that emerge from such empirical studies will need to be further refined in fundamental (as well as in experimental) studies of the liquid state.

In concluding this review I should like to propose some further studies to be carried out by either empirical or fundamental calculations on small molecular clusters and bulk liquids or dense gases of basically ionic compounds. My first proposal concerns the exploration, to be carried out with the help of the deformation dipole model, of the clusters that are formed under pressure in NaCl vapours as their density is increased both in the subcritical and supercritical regions. Such an exploration should also examine the formation of linear and low-coordinated structures in the conjectured analogy of behaviour with the expanded liquid alkali metals. Secondly, and again using an empirical interionic potentials approach, it would be interesting to explore the state of structural order in a liquid of short rods such as $HgCl_2$ and to examine how it varies over a broad region of the thermodynamic pressure-temperature plane.

Within an approach using instead fundamental quantum-mechanical calculations I would suggest two other topics for further study. Firstly, one could examine how the metal-halogen and halogen-halogen coordinations change as the size of small clusters of $ZnCl_2$ is increased. The most interesting questions concern the range of stability of the linear polymers against that of three-dimensional clusters and how their ratio approaches the ideal tetrahedral value that obtains in the bulk liquid. Finally, the comparative study of different valence states (such as in small clusters of $HgCl_2$ in comparison with HgCl, or of $AuCl_3$ in comparison with AuCl) seems to have received only low attention in the literature.

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