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STRUCTURE AND DYNAMICS OF CHARGED FLUIDS
(Lectures I and II)

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1. INTRODUCTION.

"Charged fluids" is a generic name for a vast variety of gazeous or liquid systems containing charged particles like positive or negative ions and radicals, chaged polymers, and free electrons. Systems of charged particles occur in many fields of physics and chemistry, ranging from astrophysics and plasma physics, to electrochemistry and colloid science. The common link between all these widely different systems is the predominance of long-ranged Coulomb interactions between the charged particles which confer to these systems a certain number of characteristic collective properties not found in fluids of neutral atoms or molecules. The present lectures are devoted to an overview of the essential structural and dynamical properties of some charged fluids which are of importance in condensed matter and chemical physics. This does exclude the very important field of plasma physics, although contact will be made with concepts as well as simple models borrowed from that field. We shall in fact be essentially concerned with ionic liquids and solutions, but some reference will be made to more "exotic" systems like macromolecular ionic systems and two-dimensional Coulomb fluids.

The properties of these charged fluids will be examined from an essentially microscopic point of view, within the frame-work of Statistical Mechanics. Whenever possible the results of theoretical analysis and calculations will be confronted with experimental probes of the microscopic structure and dynamics. We shall restrict ourselves to the essential features of the charged fluids under consideration, without going into the details of quantitative determinations of the properties of specific fluids. This means that, in order to gain a qualitative understanding of basic physical mechanisms, we shall give the preference to simplified models (which still retain the essential features) over very "realistic" calculations which, in any case, always hinge on a precise knowledge of inter-molecular forces.

1.1. Classes of charged fluids.

Any classification of material systems is in some sense arbitrary, but for the sake of clarity we list here the various coulombic fluids which will be considered in greater or lesser detail during these lectures.

a) Liquid metals will be looked upon as "cold" two-component plasmas, made up of positive ions and degenerate conduction (or valence) electrons. We shall restrict ourselves to metals having simple band-structures (essentially alkali metals) and their alloys. Electrical and thermal conductivities are electronic in character, with electrical conductivities σ of the order of $10^4\ \Omega^{-1}\ \mathrm{cm}^{-1}$. Some liquid alloys made up two metallic elements become ionic (with conductivities of the order of $1\ \Omega^{-1}\ \mathrm{cm}^{-1}$) at a definite stoïchiometric composition ; the equimolar Cs-Au alloy is the best - known example of such ionic melts.

b) A second class of ionic liquids comprises molten salts , made up of two ionic species of opposite charge. Salts are characterized by large Coulomb binding and a correspondingly high melting temperature and by ionic conductivities of the order of $1\ \Omega^{-1}\ \mathrm{cm}^{-1}$ in the liquid phase. At supercritical temperatures these systems exhibit a continuous change from an insulating (molecular) vapour to a dense conducting fluid. Certain crystalline salts exhibit very high conductivities, typical of the molten phase ; these are the so called super-ionic conductors, in which, putting it very schematically, one of the sublattices (corresponding generally to, the smaller ionic species) melts, while the opposite ionic species maintains crystalline long range order. The best known example is silver iodide (α-Ag I) where the Ag^+ ions are delocalized in the temperature range ($450 < T < 850$ K).

c) Metal salt solutions of the form M - MX (with M an alkali metal and X a halide) are very interesting combinations of the two former classes which generally exhibits a miscibility gap and a rapid transition from an ionic to a metallic behaviour with increasing metal concentration.

d) All preceding classes of charged fluids are exclusively made up of particles carrying an electric charge (ions and free electrons). In the direction of increasing complexity we consider next the very broad class of ionic solutions consisting of a solvent (made up of polar molecules) and a solute (made up of at least two species of oppositely charged ions). If both species of ions are of similar size and absolute charge, one deals with an electrolyte solution (e.g. $Na^+ Cl^-$ in water). Macromolecular ionic solutions contain macroions (charged polymer chains or coils, micelles,charged colloidal particles, ...) and microscopic counterions ; important members of this class of complex ionic liquids are the polyelectrolytes and the charged colloidal suspensions which play an important role in biochemistry and in many other fields.

e) Electron layers at the surface of liquid Helium and in MOS devices are two dimensional charged fluids which are being extensively studied in the laboratory ; they will be briefly considered in the last lecture.

1.2. Some important physical parameters.

We consider a charged fluid made up of ν species of particles of mass m_α ($1 \le \alpha \le \nu$), carrying an electric charge $Z_\alpha e$ (e being the elementary proton charge) ; let $n_\alpha = N_\alpha / \Omega$ be the number-density (number of particles per unit volume) of species α . Overall electroneutrality requires that

$$\sum_{\alpha=1}^{\nu} n_\nu Z_\nu = 0 \qquad (1.1)$$

A characteristic feature common to alle Coulombic fluids is the phenomenon of screening : the electric potential due to any local excess charge is effectively reduced at large distances by a rearrangement of the surrounding charges. For sufficiently low densities and high temperatures (i.e. in the weak coupling limit), this mechanism is characterized by the Debye screening lengh λ_D ; with each ionic species one associates a partial Debye wave-number :

$$k_{D_\alpha} = (4 \pi n_\alpha Z_\alpha^2 e^2 / \epsilon k_B T)^{1/2} \qquad (1.2)$$

in terms of which the screening length is given by :

$$\lambda_D^2 = \sum_\alpha k_{D\alpha}^{-2} \qquad (1.3)$$

In equation (1.2) ε is the dielectric constant of the medium in which the charges move (e.g. the solvent). The classical formula (1.2) does not apply to the degenerate gas of conduction electrons in metallic liquids.

The Debye length allows a rough distinction between two important classes of ionic liquids. Let $n = \sum n_\alpha$ be the total number density (irrespective of species) and

$$a = (3/4\pi n)^{1/3} \qquad (1.4)$$

The mean "ion sphere" radius. A third relevant length on a microscopic scale is the ionic diameter d ; the corresponding packing fraction is defined as :

$$\eta = \frac{1}{6} \pi n d^3 \qquad (1.5)$$

A convenient Coulombic coupling constant is the dimensionless parameter

$$\Gamma = \frac{Z^2 e^2}{a k_B T} \qquad (1.6)$$

where Z is some mean ionic valence. Under typical molten salt conditions ($T \simeq 10^3$K, $\mathcal{E} = 1$) one finds that

$$\lambda_D < a \simeq d \quad ; \quad \eta \simeq 0.4 \quad ; \quad \Gamma \gtrsim 50$$

This corresponds to the stong coupling regime, where Debye screening loses its physical significance, and the microscopic fluid structure is dominated by short-range order effects.

In a dilute (10^{-3} molar say) electrolyte on the other hand, the following double inequality holds ($T \simeq 300$K, $\mathcal{E} = 80$ in water) :

$$d < a < \lambda_D \quad ; \quad \eta \simeq 10^{-3} \quad ; \quad \Gamma \simeq 10^{-1}$$

which corresponds to weak coupling conditions that are correctly described by the classical Debye-Hückel theory [1]. Concentrated electrolyte solutions (e.g. 1 molar) are somewhat intermediate between the two preceding cases.

In simple metals and alloys, the screening is essentially governed by the degenerate conduction electrons and the relevant screening length is roughly equal to the Thomas-Fermi length of an ideal Fermi gas, i.e. :

$$\lambda_{TF} = \frac{1}{2}\left(\frac{\pi}{3}\right)^{1/6}\left(\frac{\hbar^2}{m_e e^2 n_e^{1/3}}\right)^{1/2} \qquad (1.7)$$

where the index e refers to electronic properties. Under typical liquid metal conditions, $\lambda_{TF} \simeq a$ and $\Gamma \simeq 200$, which corresponds to very strong coupling.

1.3. Simple models.

The simplest, although somewhat artificial model of a Coulombic fluid is the so called "one component plasma" (OCP) , a system of N point particles of charge Ze and mass m immersed in a neutralizing uniform background of opposite charge density ; the total potential energy V_N of a periodic OCP in a volume Ω includes particle-particle, particle-background and background-background terms, and can be expressed in terms of the Fourier components of the microscopic particle density :

$$\rho_{\vec{k}} = \sum_{i=1}^{N} e^{i\vec{k}\cdot\vec{r}_i}$$

in the compact form :

$$V_N(\Omega) = \frac{1}{\Omega}\sum_{\vec{k}}{}' \frac{4\pi Z^2 e^2}{k^2}\left[\rho_{\vec{k}}\rho_{\vec{k}}^* - N\right] \qquad (1.8)$$

omission of the $\vec{k} = \vec{0}$ Fourier component (denoted by a prime in the summation) accounts for the neutralizing background, while the substraction of N corresponds to the omission of the infinite self energy of the point particles.

Under the name of "jellium" the OCP has been widely used as a model for the degenerate electron gas in solids under the assumption that the ionic charge distribution is uniformly "smeared out" over the whole volume. We shall be more concerned with the opposite, high temperature limit where the classical ions are represented by the discrete point charges, while the uniform background is provided by the degenerate Fermi gas of conduction electrons. This assumption is closest to reality at high densities, since the ratio of the electron screening length (1.7) over the ion -sphere radius (1.4) can be cast in the form :

$$\frac{\lambda_{TF}}{a} = \left(\frac{\pi}{12 Z}\right)^{1/3} r_s^{-1/2} \qquad (1.9)$$

where $r_s = a/(Z^{1/3}a_0)$ is the usual electron density parameter and $a_0 = \hbar^2/m_e e^2$ is the Bohr radius. Eq.(1.9) show that in the high density limit ($r_s \ll 1$), the electron screening length becomes much larger than the inter-ionic spacing ; this means that the Pauli principle inhibits the polarization of the electron gas by the ionic charge distribution, so that the former reduces essentially to a rigid uniform background. Such extreme situations are in fact achieved in very dense degenerate stars (e.g. white dwarfs), but we shall see that the OCP is in fact a very useful starting point for the study of liquid metals. The model has the simplifying feature (which it shares with all systems of particles interacting via inverse-power potentials) that all its static and dynamical properties, when properly reduced to a dimensionless form, depend on a single variable, which is conveniently chosen to be the coupling constant(1.6). This property is easily verified upon inspection of any equilibrium statistical average, by noting that in the Boltzmann factor the ratio of the Coulomb potential over the thermal energy can be written as :

$$\frac{v(r)}{k_B T} = \frac{Z^2 e^2}{r k_B T} = \frac{Z^2 e^2}{a k_B T}\,\frac{a}{r} = \frac{\Gamma}{x} \qquad (1.10)$$

Two extensions of the OCP model are particularly useful. If finite size effects of the ions are important, a model of charged hard spheres (of diameter d) in a uniform background might be more appropriate. The situations where the background penetrates the spheres and where it is excluded, but uniform outside the spheres, can be shown to be equivalent [2]. A thermodynamic state of this model is characterized by two independent variables, which are conveniently chosen to be η and Γ.

The second extension of the OCP model corresponds to the case where there are several ionic species immersed in the neutralizing background. The binary case ("binary ionic mixture" or BIM model) has been extensively studied ; the two relevant variables are generally chosen to be Γ and one of the concentrations :

$$x_\alpha = \frac{n_\alpha}{n} \qquad ; \quad \alpha = 1, 2$$

The BIM model can be taken as a starting point for the description of binary alloys.

The simplest model retaining the essential features of ionic liquids (molten salts or electrolytes) is the "primitive model" of oppositely charged hard spheres. Let $Z_\alpha e$ and d_α be the charges and diameters of the two ionic species ; the three pair potentials are of the form :

$$v_{\alpha\beta}(r) = \begin{cases} \infty & ; \; r < d_{\alpha\beta} = \frac{1}{2}(d_\alpha + d_\beta) \\ \frac{Z_\alpha Z_\beta}{\varepsilon r} & ; \; r > d_{\alpha\beta} \end{cases} \qquad (1.11)$$

The impenetrable hard core accounts for the sharply repulsive forces acting between ions at short distances ; the Coulomb interaction is repulsive for ions of the same species and attractive for ions of opposite species. In a molten salt $\varepsilon = 1$, while for electrolytes $\varepsilon > 1$ accounts for the solvent which reduces the Coulomb interaction between ions ; notice that in this model the discrete molecular nature of the solvent is ignored and the latter is modeled by a dielectric continuum.

The "restricted primitive model" (RPM) is a symmetrical version of the primitive model in which the ions have equal diameters ($d_1 = d_2 = d$) and opposite charges ($Z_1 = - Z_2$) ; eq. (1.1) implies then $n_1 = n_2$. A thermodynamic state is characterized by the two variables η and Γ or

$$\gamma = \frac{Z^2 e^2}{\varepsilon d k_B T} = \frac{\Gamma}{2\eta^{1/3}} \qquad (1.12)$$

The various models introduced in this section must be looked upon as starting points for a qualitative understanding of charged fluids, but they are generally too crude for a quantitative description of such fluids ; more "realistic" potential models are required for this task.

1.4. Some experimental tools.

Charged fluids can be studied in the laboratory by a variety of experimental techniques which yield information on thermodynamic properties, microscopic structure and dynamics and transport coefficients. The experiments on molten salts are complicated by high temperature conditions.

We only mention here the radiation scattering techniques which give direct information on static structure and single particle or collective dynamics. X - ray and inelastic neutron scattering techniques have been reviewed by professor Enderby. The technique of isotopic substitution is crucial for the separation of partial structure factors in multi-component fluids like molten salts or aqueous solutions. Laser light scattering in conjunction with photon correlation techniques has recently yielded a wealth for information on macromolecular ionic solutions and colloidal suspensions. These experiments are capable of probing the short range order as well as the collective and self diffusion in macroionic solutions, because the macroions have a size comparable to the wavelength of the laser light.

Among the most powerful tools for the investigation of microscopic structure and dynamics are computer "experiments", i.e. simulations of small, generally periodic, samples of model fluids. The two basic Statistical Mechqnics simulation methods are the so called Metropolis Monte Carlo (MC) scheme and the "Molecular Dynamics" technique. Both methods are used to simulate systems of $N = 10^2 - 10^3$ particles interacting through given, generally pair-wise additive forces. The MC method yields exclusively static properties of either classical or degenerate systems, while the MD method is used to calculate static as well as dynamical (i.e. time-dependent) properties for classical systems.Both techniques have been abundantly described in the literature (see e.g. ref [3]). Since we shall constantly refer to results from MD simulations throughout these lectures, we briefly recall that this method amounts to solving numerically Newton's 3N coupled equations of motion :

$$\ddot{\vec{r}}_i(t) = \frac{1}{m_i}\vec{F}_i(t) = \frac{1}{m_i}\sum_{j(\neq i)}\vec{F}_{ij}(t) \qquad (1.13)$$

by a finite difference algorithm ; in equation (1.13) the dots indicate differenciation with respect to time and $\vec{F}_{ij}(t) = -\vec{F}_{ji}(t)$ is the force acting between particles i and j at time t. A widely used finite difference scheme to solve the equations of motion is the "leap-frog" algorithm, based on a straightforward Taylor expansion of $r_i(t \pm \Delta t)$ [4] :

$$\vec{r}_i(t+\Delta t) = -\vec{r}_i(t-\Delta t) + 2\vec{r}_i(t) + (\Delta t)^2\frac{1}{m_i}\sum_{j(\neq i)}\vec{F}_{ij}(t) + O(\Delta t)^4 \qquad (1.14)$$

where Δt is a judiciously chosen time increment, which must be a small fraction of the shortest characteristic time governing the particle dynamics in order to ensure a good conservation of the total energy and momentum of the system. The relevant statistical ensemble is the microcanonical ensemble (fixed total energy) and time averages of selected quantities are taken by following the trajectories of all particles over typically $10^3 - 10^5$ iterations of the basic algorithm (1.14) ; an estimate of the statistical average of any dynamical variable $A(t) = A(\vec{r}_1(t),\ldots\vec{r}_N(t);\vec{p}_1(t),\ldots\vec{p}_N(t))$ is given by :

$$\langle A \rangle = \lim_{\tau\to\infty}\frac{1}{\tau}\int_0^{\tau} A(t)\,dt \simeq \frac{1}{\mathcal{N}\cdot\Delta t}\sum_{n=1}^{\mathcal{N}} A(n\cdot\Delta t) \qquad (1.15)$$

where $\mathcal{N}$ is the total number of time steps (iterations) generated during the simulation. In particular the mean temperature is estimated from the time-average of the total kinetic energy of the system.

Surface effects, which would be severe for samples of the size tractable by present day computers ($N < 10^4$ particles), are generally eliminated by the use of periodic boundary conditions. The simulations yield then "exact" results (except for statistical uncertainties) for infinite periodic systems of particles interacting via a specified force law. The comparison with the predictions of approximate theories is then unambiguous, whereas a direct comparison between approximate theories and experimental data is always limited by our incomplete knowledge of interatomic forces.

2. MICROSCOPIC STRUCTURE AND THERMODYNAMICS.

In this lecture we introduce the fundamental static (equal time) density-density correlation functions and various related quantities ; we recall their relationship with thermodynamics and with the static linear response to external perturbations which will allow us to derive the long wave lenght behaviour of the static structure factors. Finally we sketch some theoretical techniques for the computation of static correlation functions.

2.1. Distribution functions and structure factors.

Consider a fluid made up of ν particle species, with number densities n_α and concentrations $x_\alpha = n_\alpha / n$ $(1 \leq \alpha \leq \nu)$
With each species we associate the microscopic density :

$$\rho_\alpha(\vec{r},t) = \sum_{i=1}^{N_\alpha} \delta(\vec{r} - \vec{r}_{i\alpha}(t)) \tag{2.1}$$

and its Fourier components :

$$\rho_{\vec{k}\alpha}(t) = \sum_{i=1}^{N_\alpha} e^{i\vec{k}\cdot\vec{r}_{i\alpha}(t)} \tag{2.2}$$

where $\vec{r}_{i\alpha}$ (t) denotes the center of mass position of particle i of species α at time t. Since we are interested in static (equal-time) correlations in a fluid in thermodynamic equilibrium (which satisfies time translation invariance), we may ignore at present any explicit time dependence. The one-particle densities are defined as the statistical averages (e.g. in the canonical ensemble) of the corresponding microscopic densities :

$$\rho_\alpha^{(1)}(\vec{r}) = \langle \rho_\alpha(\vec{r}) \rangle = N_\alpha \langle \delta(\vec{r} - \vec{r}_{1\alpha}) \rangle \tag{2.3}$$

the two-particle density matrix is defined in terms of the density-density correlation matrix by :

$$\begin{aligned} \rho_{\alpha\beta}^{(2)}(\vec{r},\vec{r}\,') &= \langle \rho_\alpha(\vec{r})\rho_\beta(\vec{r}\,') \rangle - \rho_\alpha^{(1)}(\vec{r})\delta_{\alpha\beta}\delta(\vec{r}-\vec{r}\,') \\ &= \sum_i {\sum_j}' \langle \delta(\vec{r}-\vec{r}_{i\alpha})\delta(\vec{r}\,'-\vec{r}_{j\beta}) \rangle \end{aligned} \tag{2.4}$$

where the prime in the summation means that the "self" term (i = j) is to be left out if $\alpha = \beta$.

For a rotationnally and translationally invariant (i.e. isotropic and homogeneous) fluid :

$$\rho_\alpha^{(1)}(\vec{r}) = n_\alpha \tag{2.5a}$$

$$\rho_{\alpha\beta}^{(2)}(\vec{r},\vec{r}\,') = n_\alpha n_\beta g_{\alpha\beta}(|\vec{r}-\vec{r}\,'|) \tag{2.5b}$$

where the $g_{\alpha\beta}$ are the (center of mass) pair distribution functions (p.d.f.). Clearly $4\pi n_\beta g_{\alpha\beta}(r)r^2dr$ is the mean number of particles of species β situated at a distance r (within dr) of a particle of species α . For $r \to \infty$, the positions of two particles in a fluid are completely decorrelated (no long-range order !) so that :

$$\lim_{r\to\infty} g_{\alpha\beta}(r) = 1 \tag{2.6}$$

It is customary to define the pair correlation functions :

$$h_{\alpha\beta}(r) = g_{\alpha\beta}(r) - 1 \tag{2.7}$$

which vanish in the limit $r \to \infty$.

In the low density (weak coupling) limit, only positions of pairs of particles are correlated, so that :

$$\lim_{n\to\infty} g_{\alpha\beta}(r) = \exp\{-v_{\alpha\beta}(r)/k_BT\} \tag{2.8}$$

where $v_{\alpha\beta}(r)$ denotes tha pair potential between species α and β (assumed to be spherical).

Two related correlation function matrices are :

$$S_{\alpha\beta}(r) = \delta_{\alpha\beta}\,\delta(\vec{r}) + n(x_\alpha x_\beta)^{1/2} h_{\alpha\beta}(r) \tag{2.9}$$

and its inverse, defined by the relation :

$$\sum_\gamma \int S^{-1}_{\alpha\gamma}(\vec{r}-\vec{r}\,'')\, S_{\gamma\beta}(\vec{r}\,''-\vec{r}\,')\, d^3r'' = \delta_{\alpha\beta}\,\delta(\vec{r}-\vec{r}\,') \tag{2.10}$$

The inverse defines the <u>direct correlation functions</u> $c_{\alpha\beta}(r)$ via :

$$S^{-1}_{\alpha\gamma}(r) = \delta_{\alpha\beta}\,\delta(\vec{r}) - n(x_\alpha x_\beta)^{1/2} c_{\alpha\beta}(r) \tag{2.11}$$

Inserting eqs.(2.9) and (2.11) into (2.10) we find that the $h_{\alpha\beta}(r)$ can be expressed in terms of the $c_{\alpha\beta}(r)$ by the Ornstein-Zernike (OZ) relations :

$$h_{\alpha\beta}(r) = c_{\alpha\beta}(r) + n \sum_\gamma c_{\alpha\gamma} \otimes h_{\gamma\beta} \tag{2.12}$$

where $\otimes$ denotes a convolution product. Introducing dimensionless Fourier transforms :

$$\hat{f}(k) = n \int e^{i\vec{k}\cdot\vec{r}} f(r)\, d^3r \tag{2.13}$$

the OZ relations take on a simple form in k-space :

$$\hat{h}_{\alpha\beta}(k) = \hat{c}_{\alpha\beta}(k) + \sum_\gamma x_\gamma\, \hat{c}_{\alpha\gamma}(k)\, \hat{h}_{\gamma\beta}(k) \tag{2.14}$$

It is easily verified that the partial structure factors :

$$S_{\alpha\beta}(k) = \frac{1}{(N_\alpha N_\beta)^{1/2}} \langle \rho_{\vec{k}\alpha}\, \rho^*_{\vec{k}\beta} \rangle \tag{2.15}$$

are précisely the Fourier transforms of the $S_{\alpha\beta}(r)$:

$$S_{\alpha\beta}(k) = \delta_{\alpha\beta} + (x_\alpha x_\beta)^{1/2}\, \hat{h}_{\alpha\beta}(k) \tag{2.16a}$$

$$S^{-1}_{\alpha\beta}(k) = \delta_{\alpha\beta} - (x_\alpha x_\beta)^{1/2}\, \hat{c}_{\alpha\beta}(k) \tag{2.16b}$$

The $S_{\alpha\beta}(k)$ are directly accessible by radiation diffraction techniques, through their linear combinations :

$$I(\theta) \sim \sum_\alpha \sum_\beta f_\alpha f_\beta S_{\alpha\beta}(k) \tag{2.17}$$

where f_α denotes the (k-dependent) atomic form factor (X-ray diffraction) or the mean nuclear scattering length (neutron diffraction) of species α , and $I(\theta)$ is the scattered intensity per unit volume, with the scattering angle given by :

$$k = 2\pi \sin\theta / \lambda$$

λ being the radiation wavelength.

2.2. <u>Number, concentration and charge structure factors.</u>

In order to illustrate the définitions of the preceding section, we now restrict ourselves to systems containing two ionic species and consider two important classes of such binary fluids : molten salts and metallic binary alloys. If n_α ($\alpha = 1,2$) denotes the partial densities of the two ionic species, the two classes of fluids differ fundamentally in that the partial densities cannot be varied independently in the molten salt, due to the electroneutrality condition (1.1), while in the alloy charge neutrality is achieved by the conduction electrons, so that n_1 and n_2 can be varied freely ; an equivalent set of independent parameters in the latter case are the total ionic number density $n = n_1 + n_2$ and one of the concentrations, $x_\alpha = n_\alpha / n$ ($x_1 + x_2 = 1$)

If one now examines typical neutron scattering or computer simulation data for the three partial structure factors of such binary systems, one is immediately struck by a fundamental difference between molten salts and binary alloys. In the case of molten alkali halides (say Na^+Cl^-), the three $S_{\alpha\beta}(k)$ exhibit a first extremum at about the same wave-number ($k \simeq 1.4$ Å^{-1} for Na Cl [5,6]), but while this corresponds to a sharp maximum for $S_{++}(k)$ and $S_{--}(k)$, the cross factor $S_{+-}(k)$ has a pronounced (negative) minimum at the same wavenumber. In the case of a liquid alloy on the other hand, the three partial structure factors exhibit sharp maxima at <u>different</u> wave-numbers (see e.g. the classic example of the copper-tin alloy $Cu_6\,Sn_5$ [7]).

In order to analyse this significant qualitative difference, it is physically instructive to consider certain linear combinations of the partial microscopic densities (2.1). The total microscopic number density is just the sum :

$$\rho_N(\vec{r},t) = \rho_1(\vec{r},t) + \rho_2(\vec{r},t) \tag{2.18}$$

In the case of the molten salt, we define the charge density :

$$\rho_Z(\vec{r},t) = Z_1\,\rho_1(\vec{r},t) + Z_2\,\rho_2(\vec{r},t) \tag{2.19}$$

From (2.18) and (2.19) we can define the following three structure factors :

$$S_{NN}(k) = \frac{1}{N}\langle \rho_{\mathbf{k}N}\,\rho^*_{\mathbf{k}Z}\rangle = \sum_\alpha \sum_\beta (x_\alpha x_\beta)^{1/2} S_{\alpha\beta}(k) \tag{2.20a}$$

$$S_{NZ}(k) = \frac{1}{N}\langle \rho_{\mathbf{k}N}\,\rho^*_{\mathbf{k}Z}\rangle = \sum_\alpha \sum_\beta (x_\alpha x_\beta)^{1/2} Z_\beta\, S_{\alpha\beta}(k) \tag{2.20b}$$

$$S_{ZZ}(k) = \frac{1}{N}\langle \rho_{\mathbf{k}Z}\,\rho^*_{\mathbf{k}Z}\rangle = \sum_\alpha \sum_\beta (x_\alpha x_\beta)^{1/2} Z_\alpha Z_\beta\, S_{\alpha\beta}(k) \tag{2.20c}$$

These structure factors are shown in ref. 6 in the case of molten Na Cl. $S_{NN}(k)$ turns out to be a relatively structureless function of k, due to a considerable amount of cancelletion between the $S_{\alpha\beta}(k)$, whereas the linear combination (2.21c) strongly enhances the structure and yields a pronounced peak in $S_{ZZ}(k)$ ($S_{ZZ}(k_{max}) \simeq 4.5$!). This is a clear manifestation of <u>charge ordering</u> in the molten salt, which becomes very apparent if one looks at the partial pair distribution functions $g_{\alpha\beta}(r)$. Computer simulations on molten alkali halides [8,9,6] show that, while $g_{++}(r) \simeq g_{--}(r)$, the oscillations of $g_{+-}(r)$ are exactly out of phase with those in $g_{++}(r)$. Consequently the linear combination $g_{NN}(r)$ is a very "flat" function of r leading to a rather structureless $S_{NN}(k)$, while the combination $g_{ZZ}(r)$ enhances the oscillations, yielding a pronounced main peak in $S_{ZZ}(k)$. Local charge neutrality is most efficiently achieved by a regular alternation of opposite and equal sign neighbour shells, which clearly manifests itself in the peculiar structure of the $g_{\alpha\beta}(r)$. Moreover the short range order is not unlike that found in a solid Na Cl structure, with an average nearest neighbour coordination number close to 6.

In the case of a binary alloy, on the other hand, we define, in addition to the microscopic number density (2.18), the microscopic deviation from the mean concentration (or concentration "density") [10] :

$$\rho_C(\vec{r},t) = x_2\,\rho_1(\vec{r},t) - x_1\,\rho_2(\vec{r},t) \tag{2.22}$$

Note that in view of the electroneutrality condition (1.1), the charge density (2.19) of a molten salt is similar to the concentration variable ρ_c of an alloy. The physical interpretation of this new variable is clear : if ρ_c is integrated over a small volume inside the alloy, the result is zero only if the numbers of particles of the two species inside this volume are exactly proportional to the mean (macroscopic) concentrations x_1 and x_2 ; $\rho_c(\vec{r},t)$ is hence the natural variable to study concentration fluctuations. The corresponding structure factors are, apart from (2.20a) :

$$\begin{aligned} S_{CC}(k) &= \frac{1}{N}\langle \rho_{\mathbf{k}C}\,\rho^*_{\mathbf{k}C}\rangle \\ &= x_1 x_2 \left\{ x_2\, S_{11}(k) - 2(x_1x_2)^{1/2} S_{12}(k) + x_1 S_{22}(k) \right\} \end{aligned} \tag{2.23a}$$

$$\begin{aligned} S_{NC}(k) &= \frac{1}{N}\langle \rho_{\mathbf{k}N}\,\rho^*_{\mathbf{k}C}\rangle \\ &= x_1 x_2 \left\{ S_{11}(k) - S_{22}(k) + \frac{x_2 - x_1}{(x_1 x_2)^{1/2}} S_{12}(k) \right\} \end{aligned} \tag{2.23b}$$

Note that for an ideal mixture (two species of identical, but tagged, ions) it is a trivail exercice to check that $S_{cc}(k) = x_1 x_2$ and $S_{NC}(k) = 0$ for all k.

By making the appropriate linear combinations of experimental data for the partial structure factors of a typical liquid alloy [7,10], one obtains a sharply peaked $S_{NN}(k)$ (not unlike the structure factor of a pure liquid), while $S_{CN}(k)$ and especially $S_{CC}(k)$ turn out to be relatively structureless, indicating the absence of any significant ordering ("random" alloy) in contradistinction to the charge ordering observed in the molten salt.

2.3. Relation to thermodynamics.

If the inter-particle forces are central and pair-wise additive, the total potential energy is of the form :

$$V_N = \frac{1}{2}\sum_\alpha \sum_\beta \sum_i \sum_j{}' v_{\alpha\beta}(|\vec{r}_i - \vec{r}_j|)$$

Within the framenwork of classical Statistical Mechanics, the internal energy of the fluid is then expressible in the terms of the p.d.f.'s $g_{\alpha\beta}(r)$:

$$\begin{aligned} \frac{U}{N} &= \frac{3}{2}k_B T + \frac{1}{N}\langle V_N \rangle \\ &= \frac{3}{2}k_B T + \frac{1}{2}\sum_\alpha \sum_\beta x_\alpha x_\beta n \int v_{\alpha\beta}(r) g_{\alpha\beta}(r)\, d^3r \end{aligned} \quad (2.24)$$

Similarly, the virial theorem leads immediately to the following expression for the pressure P :

$$\frac{P\Omega}{N k_B T} = 1 - \frac{1}{6}\sum_\alpha \sum_\beta x_\alpha x_\beta n \int r \frac{dv_{\alpha\beta}(r)}{dr} g_{\alpha\beta}(r)\, d^3r \quad (2.25)$$

For fluids of charged particles, the $v_{\alpha\beta}(r)$ contain the Coulombic part :

$$v^c_{\alpha\beta}(r) = \frac{Z_\alpha Z_\beta e^2}{\varepsilon r} \quad (2.26)$$

Use of the charge neutrality condition (1.1) allows then the $g_{\alpha\beta}(r)$ to be replaced by the correlation functions $h_{\alpha\beta}(r)$, so that the integrals appearing in (2.24-25) remain separately finite.

2.4. Static response and long wavelength behaviour.

It is well known that the static structure factors, which are a measure of equilibrium fluctuations, are intimately related to the static (linear) response functions (or susceptibilities) which describe the response of the system to a weak external perturbation.

Let $\Phi_\beta(\vec{r})$ be the potential of an external force field coupled to the density of particles of species β . Since we are interested in linear response, we may restrict ourselves to a single Fourier component of the potential :

$$\Phi_\beta(\vec{r}) = \phi_\beta(\vec{k})\, e^{-i\vec{k}\cdot\vec{r}}$$

The hamiltonian in the presence of the external field reads (with H_o the hamiltonian of the unperturbed system) :

$$\begin{aligned} H &= H_o + \int \Phi_\beta(\vec{r})\rho_\beta(\vec{r})\, d^3r \\ &= H_o + \phi_\beta(\vec{k})\rho^*_{\vec{k}\beta} \end{aligned} \quad (2.27)$$

We are interested in the response of the system as measured by the deviation of the Fourier component of the local density of species α (i.e. $\rho^{(1)}_\alpha(\vec{r})$) from its equilibrium value n_α :

$$\begin{aligned} \delta\rho_\alpha(\vec{k}) &= \frac{1}{\Omega}\int e^{i\vec{k}\cdot\vec{r}}\, \delta\rho_\alpha(\vec{r})\, d^3r \\ &= \frac{1}{\Omega}\left[\langle \rho_{\vec{k}\alpha}\rangle - \langle \rho_{\vec{k}\alpha}\rangle_o\right] \\ &= \frac{1}{\Omega}\left[\frac{1}{Q_N}\int \exp\left\{-\frac{1}{k_BT}\left[H_o + \phi_\beta(\vec{k})\rho^*_{\vec{k}\beta}\right]\right\}\rho_{\vec{k}\alpha}\, d\Gamma_N - \langle\rho_{\vec{k}\alpha}\rangle_o\right. \end{aligned} \quad (2.28)$$

where $d\Gamma_N$ denotes a phase space element, Q_N the partition function and the index o an equilibrium average over an ensemble of unperturbed systems. Linearization of the Boltzmann factor in (2.28) with respect to the weak external perturbation immediately yields the desired result :

$$\begin{aligned} \delta\rho_\alpha(\vec{k}) &= -\frac{1}{\Omega}\langle \rho_{\vec{k}\alpha}\rho^*_{\vec{k}\beta}\rangle \frac{1}{k_BT}\phi_\beta(\vec{k}) \\ &= -\frac{(n_\alpha n_\beta)^{1/2}}{k_B T} S_{\alpha\beta}(k)\, \phi_\beta(k) \end{aligned}$$

By identification with the defining relation for the static response function $\chi_{\alpha\beta}(k)$:

$$\delta\rho_\alpha(\vec{k}) = \chi_{\alpha\beta}(k)\phi_\beta(\vec{k})$$

we derive the static version of the (classical) fluctuation-dissipation theorem [11,3] :

$$\chi_{\alpha\beta}(k) = -\frac{(n_\alpha n_\beta)^{1/2}}{k_B T} S_{\alpha\beta}(k) \tag{2.29}$$

We are more specifically interested in the response of a fluid of rigid ions to the electric field of an external charge density having Fourier components ρ_e ($\vec{k}$) ; from Poisson's equation the corresponding electric potential is :

$$\phi_Z^e(k) = \frac{4\pi e^2}{k^2}\rho_e(k) \tag{2.30}$$

which couples to the microscopic charge density ρ_{kZ} of the fluid. The dielectric behaviour is charecterized by the charge-charge response function χ_{ZZ} (k) according to :

$$\partial\rho_Z(k) = \chi_{ZZ}(k)\,\phi_Z^e(k) \tag{2.31}$$

while the electrostrictive behaviour is measured by the response of the particle density

$$\partial\rho_N(k) = \chi_{NZ}(k)\,\phi_Z^e(k) \tag{2.32}$$

The charge response to the external charge density is also described by the inverse (longitudinal) static dielectric function :

$$\frac{1}{\varepsilon(k)} = \frac{k\cdot\vec{E}(k)}{k\cdot\vec{D}(k)} = \frac{\rho_Z(k)}{\rho_e(k)} = 1+\frac{\partial\rho_Z(k)}{\rho_e(k)} \tag{2.33}$$

where $\vec{E}$ and $\vec{D}$ denote the electric field and electric displacement vectors respectively, $\rho_Z = \rho_e + \partial\rho_Z$ is the total (i.e. external plus induced) charge density, and use was made of Poisson's equation.

Comparison of equation (2.33) with equations (2.31-32) yields the standard relation :

$$\frac{1}{\varepsilon(k)} = 1 + \frac{4\pi e^2}{k^2}\chi_{ZZ}(k) \tag{2.34}$$

while the fluctuation-dissipation theorem applied to the charge response leads to :

$$\chi_{ZZ}(k) = -\frac{n}{k_B T} S_{ZZ}(k) \tag{2.35}$$

From its definition (2.20c), the charge structure factor $S_{ZZ}(k)$ is non-negative, so that eqs. (2.34-35) entail the stability condition :

$$\frac{1}{\varepsilon(k)} < 1 \tag{2.36}$$

Negative values of the dielectric function are a common feature of strongly coupled charged fluids [12].

Inside the fluid an external charge is screened due to the polarization of the medium, and each ion experiences a local electric field which is the superposition of the external field and the field due to the induced charge density. The response of the system to the local (rather than external) electric potential is described by the screened response function :

$$\partial\rho_Z(k) = \breve{\chi}_{ZZ}(k)\left[\phi_Z^e(k) + \partial\phi_Z(k)\right] \tag{2.37}$$

where

$$\partial\phi_Z(k) = \frac{4\pi e^2}{k^2}\,\partial\rho_Z(k) \tag{2.38}$$

Confrontation of eqs. (2.31) and (2.37) yields the relation between external and screened response functions :

$$\chi_{ZZ}(k) = \frac{\breve{\chi}_{ZZ}(k)}{1 - \frac{4\pi e^2}{k^2}\breve{\chi}_{ZZ}(k)} \tag{2.39}$$

while :

$$\varepsilon(k) = 1 - \frac{4\pi e^2}{k^2}\breve{\chi}_{ZZ}(k) \tag{2.40}$$

Perfect screening in a conducting fluid imposes the condition :

$$\lim_{k\to 0}\rho_Z(k) = \lim_{k\to 0}\left[\rho_e(k) + \partial\rho_Z(k)\right] = 0 \tag{2.41}$$

which, combined with eqs. (2.31), (2.32) and (2.35), determines the long wavelength behaviour of the charge structure factor :

$$\lim_{k\to 0} \frac{k_D^2}{k^2} S_{ZZ}(k) = \overline{Z^2} \tag{2.42}$$

where :

$$\overline{Z^2} = \sum_\alpha x_\alpha Z_\alpha^2 \tag{2.43}$$

and $k_D^2 = \sum_\alpha k_{D\alpha}^2$ is the Debye wave-number defined by eqs. (1.2-3).

The charge structure factor vanishes as k^2 for long wavelengths, a consequence of the k^2 singularity of the Coulomb potential.

The partial structure factors, on the other hand, remain finite in the limit k→0. For the sake of illustration we now specifically consider the case of a binary ionic liquid. The total charge surrounding an ion of a given species must exactly cancel the charge of that ion : hence we have the electroneutrality constraints :

$$\begin{aligned} n_1 Z_1 \int g_{11}(r)\, d^3r + n_2 Z_2 \int g_{12}(r)\, d^3r &= -Z_1 \\ n_1 Z_1 \int g_{12}(r)\, d^3r + n_2 Z_2 \int g_{22}(r)\, d^3r &= -Z_2 \end{aligned} \tag{2.44}$$

Using equations (1.1) and (2.16a), in conjunction with the compressibility equation for binary fluids [13], it is then a straightforward exercice to show that the partial structure factors have the following long wavelength limit :

$$\lim_{k\to 0} |Z_\alpha Z_\beta|^{1/2} S_{\alpha\beta}(k) = n k_B T K_T \tag{2.45}$$

where $K_T = -(\partial\Omega/\partial P)_{N,T}/\Omega$ is the isothermal compressibility

We finally examine the long wavelength behaviour of the dielectric function $\mathcal{E}(k)$, restricting ourselves now, for the sake of simplicity, to the one component plasma (OCP) model for which number and charge density fluctuations coincide. A simple macroscopic calculation will give us the required long wavelength behaviour [14]. In the absence of any flow, the force due to the local electric field must be exactly cancelled by the force due to the pressure gradient :

$$n(Ze)\vec{E}(\vec{r}) = \vec{\nabla} P(\vec{r}) \tag{2.46}$$

Poisson's equation reads :

$$\vec{\nabla}\cdot\vec{E}(\vec{r}) = 4\pi e\left[\rho_e(\vec{r}) + \delta\rho_Z(\vec{r})\right] \tag{2.47}$$

Assuming local thermodynamic equilibrium, and considering an isothermal process, the pressure fluctuation can be expressed as :

$$\delta P(\vec{r}) = P(\vec{r}) - P_0 = \left(\frac{\partial P}{\partial n}\right)_T \delta n(\vec{r}) = \frac{1}{Z}\left(\frac{\partial P}{\partial n}\right)_T \delta\rho_Z(\vec{r}) \tag{2.48}$$

Combining eqs. (2.46-48) we arrive at the following differential equation for $\delta\rho_Z$:

$$\frac{1}{4\pi Z^2 e^2}\left(\frac{\partial P}{\partial n}\right)_T \nabla^2 \delta\rho_Z(\vec{r}) - \delta\rho_Z(\vec{r}) = \rho_e(\vec{r}) \tag{2.49}$$

This is easily solved in Fourier space :

$$\delta\rho_Z(\vec{k}) = -\frac{\rho_e(\vec{k})}{1 + k^2/k_s^2} \tag{2.50}$$

where

$$k_s^2 = 4\pi Z^2 e^2 n^2 K_T \tag{2.51}$$

is the square of the screening wave number. The long wavelength limit of $\mathcal{E}(k)$ follows then immediately from eq.(2.33) :

$$\mathcal{E}(k) = 1 + \frac{k_s^2}{k^2} \tag{2.52}$$

Note that the perfect screening condition (2.41) is contained in eq.(2.50). The electrostatic potential around the screened external charge is, according to Poisson's equation :

$$\begin{aligned} \phi_Z(\vec{k}) &= \frac{4\pi e^2}{k^2}\left[\rho_e(\vec{k}) + \delta\rho_Z(\vec{k})\right] \\ &= \frac{4\pi e^2}{k^2\,\mathcal{E}(k)}\rho_e(\vec{k}) = \frac{4\pi e^2}{k^2 + k_s^2}\rho_e(\vec{k}) \end{aligned}$$

If one of the point charges in the fluid is regarded as the external charge ($\rho_e(r) = Ze\delta(\vec{r})$), the preceding result shows that the effective electric potential due to that charge decays exponentially at large distances :

$$v_{eff}(r) = \frac{Z^2e^2}{r}\exp\{-k_s r\} \tag{2.53}$$

In the weak coupling limit, K_T goes over to its ideal gas limit $(nk_BT)^{-1}$ and k_s reduces to the Debye wave number k_D(eq.(1.2)). In the strong coupling regime ($\Gamma > 1$), the compressibility of the OCP becomes negative, so that k_s takes on imaginary values [14], corresponding to an oscillatory behaviour of $v_{eff}(r)$, characteristic of short range ordering.

2.5. Approximations for the pair distribution functions.

In this section we briefly examine some of the more efficient approximations for the calculation of the pair distribution functions. Again, for the sake of simplicity, we shall first restrict ourselves to the case of the simplest model ionic fluid, the OCP (with Z = 1), the pair structure of which is characterized by a single p.d.f. g(r). In the weak-coupling limit ($\Gamma \to 0$), correlations become negligible and we make the familiar "random phase" approximation (RPA), which amounts to replacing the screened response function $\chi(k)$ in eq.(2.39) by the response function of a system of non-interacting particles, $\chi_0(k)$, which reduces to $-n/k_BT$ in the classical limit. The structure factors follows then directly from (2.35) :

$$S_{RPA}(k) = \frac{k^2}{k^2 + k_D^2} \tag{2.54}$$

It is worth noting that a similar reasoning leads to the familiar Lindhard dielectric function of the degenerate electron gas [15]. $S_{RPA}(k)$ obviously satisfies the long wavelength limit (2.42). From the OZ relation (2.16b) it is immediately cleat that the RPA is equivalent to setting :

$$\hat{c}(k) = -\hat{v}(k)/k_BT = -k_D^2/k^2 \tag{2.55a}$$

or

$$c(r) = -v(r)/k_BT \tag{2.55b}$$

Eq.(2.55a) is believed to be true asymptotically ($r\to\infty$), for any pair potential [16]; the RPA replaces the direct correlation function by its asymptotic form, for all distances r.

Eq.(2.55) allows a straightforward generalization of the RPA to multi-component fluids, in conjunction with the OZ relations (2.16).

Historically the RPA was first derived by Debye and Hückel (DH) [1] from the Poisson-Boltzmann equation. The charge density around a central ion is related to the electrostatic potential by the Boltzmann factor :

$$\rho_z(r) = n\left[g(r) - 1\right] = n\left[\exp\left\{-\left[v(r) + \Phi(r)\right]/k_BT\right\} - 1\right] \tag{2.56a}$$

where $v(r) = e^2/r$ and $\Phi(r)$ are the potentials due to the central ion and to the polarization cloud respectively. The latter satisfies Poisson's equation :

$$\nabla^2 \Phi(r) = -4\pi e^2 \rho_z(r) \tag{2.56b}$$

which admits the solution :

$$\begin{aligned}\Phi(r) &= \int d^3r' \rho_z(r')\, v(|\vec{r} - \vec{r}\,'|) \\ &= n\int d^3r'\, h(r')\, v(|\vec{r} - \vec{r}\,'|)\end{aligned} \tag{2.56c}$$

where the definition (2.7) was used. The coupled equations (2.56) form a closed, non-linear set. Upon linearization of eq. (2.56a) and subsequent Fourier transformation, the RPA (orDH) structure factor (2.54) is recovered. The linearization is only justified in the weak coupling (i.e. low density or high temperature) limit. For intermediate couplings, the full, non-linear Poisson-Boltzmann equation yields reasonable result [17-18] despite the neglect of correlations between particles in the polarization cloud. These correlations are partly included in the so-called "hypernetted chain" (HNC) approximation [3,19] , which amounts to replacing the bare potential v(r) by the "renormalized" potential $- k_BT \cdot c(r)$ in eq.(2.56c). Combining eqs.(2.56) and (2.12) we cast the HNC approximation in the standard form :

$$g(r) = \exp\left\{-v(r)/k_BT + h(r) - c(r)\right\} \tag{2.57}$$

The multi-component generalization is :

$$g_{\alpha\beta}(r) = \exp\left\{-v_{\alpha\beta}(r)/k_BT + h_{\alpha\beta}(r) - c_{\alpha\beta}(r)\right\} \tag{2.58}$$

Eqs.(2.58) and (2.12) form a closed set which must be solved numerically, by an iterative procedure. Comparison with computer simulation data shows that the HNC approximation generally yields reasonable pair distribution functions for Coulombic fluids, even under strong coupling conditions (see. e.g. references 9,19-21,26). Some improved versions of the HNC scheme have recently been proposed, which lead to nearly perfect agreement with the simulation data [22,23].

Another powerful approximation scheme, which applies to systems of charged hard spheres, is the so-called "mean spherical" approximation (MSA) which has the advantage of admitting analytical solutions in some cases. The pair potentials being of the form (1.11), the MSA completes the exact requirements :

$$g_{\alpha\beta}(r) = 0 \quad ; \; r < d_{\alpha\beta} \tag{2.59a}$$

by the approximate closure :

$$c_{\alpha\beta}(r) = -v_{\alpha\beta}(r)/k_BT \quad ; \; r > d_{\alpha\beta} \tag{2.59b}$$

In the limit of vanishing hard sphere diameters (point ions), the MSA reduces to the RPA (cf.eq.2.55b) ; for finite diameters, the MSA includes short range correlations via eq.(2.59a). Eqs (2.59) together with the OZ relations (2.12) form a closed set which has been solved analytically in the case of the restricted primitive model (equal diameters, opposite charges) [24] . The extension to unequal diameters and arbitrary numbers of components is also available, but requires the numerical solution of an algebraic equation [25] . The MSA solutions reproduce the main qualitative features of the partial p.d.f.'s in the concentrated electrolyte and in the molten salt regime, and have been used to analyse X-ray and neutron diffraction data for molten alkali halides [27]. In order to achieve quantitative agreement with experimental or simulation data, one must resort to semi-emperical modifications of the original MSA scheme, but at the expense of considerable numerical complications [28,29] .