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STRUCTURE AND DYNAMICS OF CHARGED FLUIDS

(Lectures III & IV)

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3. MICROSCOPIC DYNAMICS AND TRANSPORT.

In this lecture we introduce a certain number of tools, mainly time-dependent correlation functions and their associated memory functions, which serve in a quantitative analysis of single-particle and collective motions in neutral or charged fluids, and which lead to transport coefficients within the framework of linear response theory. Many of the concepts of this lecture have already been introduced in the lectures by Gerl, and can be found in numerous textbooks or review articles [3,11,30-32] . Consequently we shall be very brief as regards generalities, and concentrate on aspects which are specific for charged fluids [12,19].

3.1. Time-dependent correlations : a brief reminder.

A microscopic dynamical variable will be any scalar, vectorial or tensorial function of the instantaneous positions and (or) momenta (or velocities) of some, or all, particles of a many-particle system. Examples are the partial microscopic densities (2.1) or their Fourier components (2.2). The time evolution of a dynamical variable A is governed by :

$$\dot{A} = \frac{dA}{dt} = iLA \tag{3.1}$$

where L denotes the Liouville operator; in Quantum Statistical Mechanics L is the commutator :

$$L = \frac{1}{\hbar}[H,\ ] \tag{3.2a}$$

while in classical Statistical Mechanics, to which we shall henceforth restrict ourselves, L is the Poisson Bracket :

$$L = i\{H,\ \} = i\sum_{j=1}^{N}\left(\frac{\partial H}{\partial \vec{r}_j}\cdot\frac{\partial}{\partial \vec{p}_j} - \frac{\partial H}{\partial \vec{p}_j}\cdot\frac{\partial}{\partial \vec{r}_j}\right) \tag{3.2b}$$

(3.1) is formally solved as :

$$A(t) = \exp\{iLt\}A \tag{3.3}$$

where $A \equiv A(o)$ denotes the initial value of the dynamical variable.

The equilibrium time correlation function (TCF) of two dynamical variables A and B is defined as :

$$\begin{aligned} C_{AB}(t',t'') &= \langle A(t')B^*(t'')\rangle \\ &= \langle A(t'-t'')B^*(0)\rangle \end{aligned} \tag{3.4}$$

where the angular brackets denote an ensemble average over the initial phase, and advantage is taken of the stationarity of equilibrium averages. More precisely, if $t = t'-t''$:

$$C_{AB}(t) = \int d^{3N}r\int d^{3N}p\,(e^{iLt}A)B^* f_o^{(N)}(\vec{r}^N,\vec{p}^N) \tag{3.5}$$

where $f_o^{(N)}$ denotes the equilibrium distribution function in 6N dimensional phase space. More generally, if the dynamical variables vary in space (like) the partial densities (2.1)), and if the fluid is homogeneous (translationally invariant in space), the corresponding TCF will also depend on the spatiale variable $\vec{r} = \vec{r}' - \vec{r}''$:

$$\begin{aligned} C_{AB}(\vec{r},t) &= \langle A(\vec{r}',t)B^*(\vec{r}'',0)\rangle \\ &= \langle A(\vec{r},t)B^*(\vec{0},0)\rangle \end{aligned} \tag{3.6}$$

It is clear that spatial homogeneity implies that only Fourier components of opposite wave numbers have non-vanishing correlations, so that :

$$\begin{aligned} C_{AB}(\vec{k},t) &= \int e^{i\vec{k}\cdot\vec{r}}\,C_{AB}(\vec{r},t) \\ &= \langle A_{\vec{k}}(t)\,B^*_{\vec{k}}(0)\rangle \end{aligned} \tag{3.7}$$

We shall only consider dynamical variables of zero mean, <A> = 0. After a sufficiently long time interval, any dynamical variable will be completely decorrelated from the initial value of the same, or any other, variable, so that :

$$\begin{aligned} \lim_{t\to\infty} C_{AB}(t) &= \langle A(t)\rangle\langle B^*(0)\rangle \\ &= \langle A\rangle\langle B^*\rangle = 0 \end{aligned} \tag{3.8}$$

This property allows us to define the spectral function (or power spectrum) of any TCF as its Fourier transform in time :

$$\hat{C}_{AB}(\omega) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} e^{i\omega t}\,C_{AB}(t)\,dt \tag{3.9}$$

It is also convenient to introduce the Laplace transform :

$$\tilde{C}_{AB}(z) = \int_0^{\infty} e^{izt}\,C_{AB}(t)\,dt\,;\quad \mathrm{Im}\,z > 0 \tag{3.10}$$

which is related to the spectrum by a Hilbert transformation :

$$\tilde{C}_{AB}(z) = i\int_{-\infty}^{+\infty} d\omega\,\frac{\hat{C}_{AB}(\omega)}{z-\omega} \tag{3.11}$$

Inversely :

$$\hat{C}_{AB}(\omega) = \lim_{\varepsilon\to 0}\frac{1}{\pi}\tilde{C}'_{AB}(\omega+i\varepsilon) \tag{3.12}$$

where the prime denotes a real part (a double prime will denote an imaginary part). If A and B are both either even or odd functions of the momenta, their TCF is an even function of time and the spectrum is an even function of frequency. $C_{AB}(t)$ admits then a Taylor expansion in even powers of t :

$$C_{AB}(t) = \sum_{n=0}^{\infty} \frac{t^{2n}}{(2n)!} C_{AB}^{(2n)}(t=0)$$
$$= \sum_{n=0}^{\infty} \frac{t^{2n}}{(2n)!} (-1)^n \langle A^{(n)}(0)\, B^{*(n)}(0) \rangle$$
$$= \sum_{n=0}^{\infty} \frac{t^{2n}}{(2n)!} \langle (L^n A)(L^n B^*) \rangle \qquad (3.13)$$

where (n) denotes an n^{th} order derivative with respect to time. Differentiating the inverse Fourier transform of eq.(3.9) 2n times with respect to t yields upon setting t = o :

$$\Omega_{AB}^{(2n)} = \int_{-\infty}^{+\infty} \omega^{2n} \hat{C}_{AB}(\omega)\, d\omega$$
$$= (-1)^n \, C_{AB}^{(2n)}(0) \qquad (3.14)$$

Thus the frequency moments of the spectral function are directly related to derivatives of the TCF taken at t = 0. The latter are static (equal time) correlation functions, similar to the static structure factors introduced in the preceding chapter. The short time expansion of $C_{AB}(t)$ in eq.(3.13) implies, via eq.(3.11), the following high frequency expansion for the Laplace transform :

$$\tilde{C}_{AB}(z) = \frac{i}{z} \sum_{n=0}^{\infty} \frac{\Omega_{AB}^{(2n)}}{z^{2n}} \qquad (3.15)$$

The exact time evolution of any dynamical variable is described by eq.(3.1). For pratical purposes, a more phenomenological approach is widely used. We start from the familiar Langevin equation for the velocity of a Brownian particle ; if u denotes one of its cartesian components, ξ the friction coefficient and R(t) a component of the stochastic random force, this equation reads :

$$m\,\dot{u}(t) = -m\xi\, u(t) + R(t) \qquad (3.16)$$

Equipartition of energy and the assumption that R(t) is orthogonal to u(o) for all t, lead to the following relation between ξ and $\vec{R}$ [11] :

$$\xi = \frac{1}{m k_B T} \int_0^{\infty} \langle R(t)\, R(0) \rangle \, dt \qquad (3.17)$$

Taking into account retarded effects and the action of an external force field X(t), eq. (3.16) is generalized to :

$$\dot{u}(t) = -\int_0^t \xi(t-s)\, u(s)\, ds + \frac{1}{m} R(t) + \frac{1}{m} X(t) \qquad (3.18)$$

Considering first the case X = 0 , projecting both sides of equation (3.18) unto the initial velocity u(0), and making the usual assumption :

$$\langle R(t)\, u(0) \rangle = 0 \quad \forall\, t \qquad (3.19)$$

we immediately derive an expression for the Laplace transform (3.10) of the velocity autororrelation function (ACF) $C_{uu}(t)$:

$$\tilde{C}_{uu}(z) = \frac{C_{uu}(t=0)}{-iz + \tilde{\xi}(z)} = \frac{k_B T/m}{-iz + \tilde{\xi}(z)} \qquad (3.20)$$

$\tilde{\xi}(z)$ is given by a generalization of equation (3.17) :

$$\tilde{\xi}(z) = \frac{1}{m k_B T} \int_0^{\infty} \langle R(t)\, R(0) \rangle e^{izt}\, dt \qquad (3.21)$$

The generalized Langevin equation (3.20) can be extended to any dynamical variable, and the generalized "random force" can be given a precise statistical Mechanics interpretation in terms of a projected time evolution [33,3] . If A denotes a set of dynamical variables, the correlation function matrix obeys the "memory" function equation" :

$$\dot{C}_{AA}(t) - i\Omega C_{AA}(t) + \int_0^t M(t-s) C_{AA}(s)\, ds = 0 \qquad (3.22)$$

where the frequency matrix Ω is given by :

$$\Omega = \langle \dot{A} A^* \rangle (\langle A A^* \rangle)^{-1}$$

and the memory function matrix M plays the role of the generalized friction coefficient ξ . Taking Laplace transforms, eq.(3.22) yields :

$$\tilde{C}_{AA}(z) = C_{AA}(t=0) \left[-iz - i\Omega + \tilde{M}(z) \right]^{-1} \qquad (3.23)$$

The practical interest of eq.(3.22) or (3.23) lies in the fact that for a judicious choice of the set of dynamical variables A, the memory functions have a simpler structure (in particular a faster decay) than the corresponding correlation functions, and are hence more easily amenable to simple relaxation-time approximations.

3.2. Mobilities and conductivities.

If an ensemble of brownian particles is initially (t=o) located at the origin, their mean square deviation in the x-direction is given by Einstein's law :

$$\langle x^2(t) \rangle = 2Dt \tag{3.24}$$

where D is the self-diffusion constant which is given by the time integral of the velocity ACF :

$$D = \int_0^\infty C_{uu}(t)dt = \tilde{C}_{uu}(z=0) \tag{3.25}$$

If a periodic external force is applied to the brownian particles (cf. eq. (3.18)) :

$$X(t) = \Re X_0 e^{-i\omega t}$$

the mean velocity at time t (which measures the response of the system to the external field) is given by :

$$\langle u(t) \rangle = \Re \mu(\omega) X_0 e^{-i\omega t} \tag{3.26}$$

where the expression for the frequency dependent mobility $\mu(\omega)$ is easily derived from eq.(3.18) :

$$\mu(\omega) = \frac{1}{m} \frac{1}{-i\omega + \xi(\omega)} = \frac{1}{k_B T} \tilde{C}_{uu}(\omega) \tag{3.27}$$

In particular the static mobility $\mu = \mu(\omega = 0)$ and the self diffusion constant D obey the Einstein relation :

$$\mu = \frac{D}{k_B T} \tag{3.28}$$

$\mu(\omega)$ is the simplest example of a linear response function (or dynamical susceptibility), and eq.(3.27) is a special case of the fluctuation-dissipation theorem [11].

These results for a particle are easily generalizable to the case of a multicomponent charged fluid. With each species we associate a velocity ACF :

$$C_\alpha(t) \equiv C_{\vec{v}_\alpha \vec{v}_\alpha}(t) = \langle \vec{v}_\alpha(t) \cdot \vec{v}_\alpha(0) \rangle \tag{3.29}$$

where $\vec{v}_\alpha$ denotes the velocity of any one of the N_α particles of species α.

The corresponding self-diffusion constant is given by :

$$D_\alpha = \frac{1}{3} \int_0^\infty C_\alpha(t)dt \tag{3.30}$$

and the (static) mobility of ions of species α follows from the Einstein relation :

$$\mu_\alpha = \frac{Z_\alpha e D}{k_B T} \tag{3.31}$$

where the factor $Z_\alpha e$ arises because we adopt the convention that the mobility measures the response of a single ion to an applied electric field rather than to the corresponding force. The collective response to a (local) periodic field is characterized by the (complex) frequency-dependent electric conductivity :

$$\sigma(\omega) = \sigma'(\omega) + \sigma''(\omega) = \frac{Ne^2}{3k_B T} \int_0^\infty e^{i\omega t} C_{zz}(t)dt \tag{3.32}$$

where $C_{zz}(t)$ is the ACF of the fluctuating microscopic charge current in the absence of an external electric field :

$$C_{zz}(t) = \frac{1}{N} \langle \vec{J}_z(t) \cdot \vec{J}_z(0) \rangle \tag{3.33a}$$

$$\vec{J}_z(t) = \sum_\alpha Z_\alpha \vec{J}_\alpha(t) \tag{3.33b}$$

$$\vec{J}_\alpha(t) = \sum_{i=1}^{N_\alpha} \vec{v}_{i\alpha}(t) \tag{3.33c}$$

The usual static electrical conductivity σ can then be identified as :

$$\sigma = \lim_{\omega \to 0} \frac{1}{V} \sigma(\omega) = \frac{\omega_p^2}{4\pi} \int_0^\infty J_z(t)dt \tag{3.34}$$

where :

$$\omega_p^2 = \sum_\alpha \omega_{p\alpha}^2 = \sum_\alpha \frac{4\pi n_\alpha Z_\alpha^2 e^2}{m_\alpha} \tag{3.35}$$

is the square of the plasma frequency, and $J_z(t) = C_{zz}(t)/C_{zz}(0)$ is the normalized ACF of the fluctuating charge current. From eqs.(3.32) and (3.35) the following sum rule for the real part of the frequency-dependent conductivity is easily verified :

$$\int_{-\infty}^{+\infty} \frac{d\omega}{\pi} \sigma'(\omega) = \omega_p^2 \tag{3.36}$$

An approximate relation between the static conductivity and the mobilities of the various ionic species follows from eqs.(3.30), (3.31) and (3.34) if all cross-correlations between the velocities of different ions (of the same or of different species) are neglected, i.e. if one assumes :

$$\langle \vec{v}_{i\alpha}(t)\cdot\vec{v}_{j\beta}(0)\rangle = 0 \quad ; \quad i \neq j$$

In classical Statistical Mechanics this assumption is exact only for t = o ; if it is generalized to all times, it leads to a simple relation between $C_{zz}(t)$ and $C_\alpha(t)$:

$$C_{zz}(t) = \sum_\alpha x_\alpha z_\alpha^2 C_\alpha(t)$$

from which the familiar Nernst-Einstein relation follows immediately :

$$\sigma = \frac{e^2}{k_B T}\sum_\alpha n_\alpha Z_\alpha^2 D_\alpha = \sum_\alpha n_\alpha Z_\alpha e \mu_\alpha \qquad (3.37)$$

This approximate relation is well verified in electrolyte solutions, but in molten alkali halides, formula (3.37) overestimates σ by typically 20%.

The formulae of this section are directly applicable to the study of ionic conductivity. In liquid metals and alloys the much larger conductivity is due to the degenerate Fermi gas of conduction electrons. For simple metals, like the alkali, the conductivity is accurately calculated from Ziman's formula in the framework of a Lorentz model, where the mutually non-interacting electrons are individually scattered by the spatially correlated ions ; the relatively weak electron-ion interaction is treated in Born approximation [34] . The resulting formula for the resistivity ($\rho = 1/\sigma$) of a liquid metal reads :

$$\rho = \frac{m_e^2}{12\pi^3\hbar^3 e^3 n_e}\int_0^{2k_F} |\hat{v}(k)|^2 S(k)\, k^3 dk \qquad (3.38)$$

where $\hat{v}(k)$ is the Fourier transform of the electron-ion pseudo-potential, S(k) is the ionic structure factor and k_F is the Fermi momentum of the electron gas. Excellent results for the temperature variation of the resistivity of liquid alkali have been obtained from eq.(3.38) on the basis of the OCP model for the static structure factor [35] .

3.3. Density and current correlation functions.

In the study of wave-number dependent collective modes, the basic dynamical variables are the Fourier components (2.2) of the partial microscopic densities, and the associated partial particle currents :

$$\vec{j}_{\vec{k}\alpha}(t) = \sum_{i=1}^{N_\alpha} \vec{v}_{i\alpha}(t)\, e^{i\vec{k}\cdot\vec{r}_{i\alpha}(t)} \qquad (3.39)$$

The two are related by the continuity equations expressing particle conservation :

$$\dot{\rho}_{\vec{k}\alpha}(t) = i\,\vec{k}\cdot\vec{j}_{\vec{k}\alpha}(t) \qquad (3.40)$$

We define the partial density TCF's :

$$F_{\alpha\beta}(k,t) = \frac{1}{(N_\alpha N_\beta)^{1/2}}\langle \rho_{\vec{k}\alpha}(t)\,\rho^*_{\vec{k}\beta}(0)\rangle \qquad (3.41)$$

which depend only on k = $|\vec{k}|$, due to the rotational invariance of an isotropic fluid. Their spectra (3.9) are the so-called dynamical structure factors :

$$S_{\alpha\beta}(k,\omega) \equiv \hat{F}_{\alpha\beta}(k,\omega)$$

The initial values of the $F_{\alpha\beta}$ are clearly the static structure factors defined in eq.(2.15) :

$$F_{\alpha\beta}(k, t=0) = S_{\alpha\beta}(k) = \int_{-\infty}^{+\infty} S_{\alpha\beta}(k,\omega)\, d\omega \qquad (3.42)$$

From eqs.(3.14) and (3.40) it is immediately clear that the dynamical structure factors obey the f - sum rules :

$$\Omega^{(2)}_{\alpha\beta}(k) = \int_{-\infty}^{+\infty}\omega^2 S_{\alpha\beta}(k,\omega)\, d\omega = \frac{k^2}{(N_\alpha N_\beta)^{1/2}}\langle j^{(x)}_{\vec{k}\alpha}\, j^{(x)*}_{\vec{k}\beta} \qquad (3.43)$$

$$= k^2 v_{o\alpha}^2 \delta_{\alpha\beta}$$

where $v_{o\alpha}$ denotes the thermal velocity $(k_B T/m_\alpha)^{1/2}$. The longitudinal and transverse partial current TCF's are defined in terms of the projections of $\vec{j}_{\vec{k}\alpha}(t)$ parallel and perpendicular to the wave vector $\vec{k}$:

$$C^L_{\alpha\beta}(k,t) = \frac{1}{(N_\alpha N_\beta)^{1/2} k^2}\langle \vec{k}\cdot\vec{j}_{k\alpha}(t)\ \vec{k}\cdot\vec{j}^{\,*}_{\vec{k}\beta}(0)\rangle \qquad (3.44a)$$

$$C^T_{\alpha\beta}(k,t) = \frac{1}{(N_\alpha N_\beta)^{1/2} k^2}\,\mathrm{Tr}\left\{\langle [\vec{k}\wedge\vec{j}_{\vec{k}\alpha}(t)][\vec{k}\wedge\vec{j}^{\,*}_{\vec{k}\beta}(0)]\rangle\right\} \qquad (3.44b)$$

From the continuity equations (3.40) we immediately deduce :

$$C^L_{\alpha\beta}(k,t) = -\frac{1}{k^2}\frac{d^2}{dt^2}F_{\alpha\beta}(k,t) \qquad (3.45)$$

so that the $C^L_{\alpha\beta}$ do not contain any new information. The $C^T_{\alpha\beta}$ are, however, independent functions, since the tranverse currents are completely decoupled from the longitudinal currents.

3.4. Concentration fluctuations.

In many situations, certain linear combinations of the partial densities or currents have a physically more transparent significance, as was already stressed in section 2.2 for static fluctuations. For binary mixtures and alloys we have introduced the variables ρ_N and ρ_c defined by eqs.(2.18) and (2.22). The corresponding number-number, number-concentration and concentration-concentration dynamical structure factors are linear combinations of the $S_{\alpha\beta}(k,\omega)$ which are obvious generalizations of eqs.(2.23).

The hydrodynamic (i.e. small k and ω) limit of $S_{cc}(k,\omega)$ can be easily inferred from the macroscopic Fick's law :

$$\vec{j}_c(\vec{r},t) = -D\vec{\nabla}\rho_c(\vec{r},t) \tag{3.46}$$

where $\vec{j}_c = x_2\vec{j}_1 - x_1\vec{j}_2$ is the interdiffusion current, D is the (mutual) diffusion constant and ρ_c is the local concentration variable which is also related to $\vec{j}_c$ by the continuity equation :

$$\dot{\rho}_c(\vec{r},t) + \vec{\nabla}\cdot\vec{j}_c(\vec{r},t) = 0 \tag{3.47}$$

It should be noted that on a macroscopic scale, the local variables ρ_c and $\vec{j}_c$ are averages of the corresponding microscopic variables over a small (but macroscopic) volume element of the fluid. Eliminating $\vec{j}_c$ between eqs.(3.46-47) we obtain a closed equation for ρ_c :

$$\dot{\rho}_c(\vec{r},t) = D\nabla^2\rho_c(\vec{r},t) \tag{3.48a}$$

or

$$\dot{\rho}_c(\vec{k},t) = -k^2 D\rho_c(\vec{r},t) \tag{3.48b}$$

Going to Laplace transforms we obtain :

$$\tilde{\rho}_c(\vec{k},z) = \frac{\rho_c(\vec{k},t=0)}{-iz + Dk^2} \tag{3.49}$$

The long wave-length, low frequency concentration correlation function reads then :

$$\tilde{F}_{cc}(k,z) = \frac{1}{N}\langle\tilde{\rho}_c(\vec{k},z)\,\rho_c^{*}(\vec{k},t=0)\rangle = \frac{1}{N}\langle|\rho_c(\vec{k},0)|^2\rangle\left[-iz + Dk^2\right]^{-1} \tag{3.50}$$

In the small k limit we have [13] :

$$S_{cc}(k) = \frac{1}{N}\langle|\rho_c(\vec{k},0)|^2\rangle \underset{k\to 0}{=} \left[\frac{\partial^2 g}{\partial x_1^2}\right]^{-1}_{T,P,N} \tag{3.51}$$

where $g = G/Nk_BT$ denotes the reduced Gibbs free energy per ion. In the "hydrodynamic limit", the resulting dynamical structure factor is :

$$S_{cc}(k,\omega) = \frac{1}{\pi}\tilde{F}'_{cc}(k,z=\omega) = \frac{1}{\pi}\left(\frac{\partial^2 g}{\partial x_1^2}\right)^{-1}\frac{Dk^2}{\omega^2 + (Dk^2)^2} \tag{3.52}$$

(3.52) shows that the mutual diffusion constant can be calculated from the limit :

$$D = \pi\left(\frac{\partial^2 g}{\partial x_1}\right)\lim_{\omega\to 0}\lim_{k\to 0}\frac{\omega^2}{k^2}S_{cc}(k,\omega) \tag{3.53}$$

Remembering eq.(3.44a) this relation can be cast in a standard Kubo form, similar to eq.(3.34) for the conductivity :

$$D = \left(\frac{\partial^2 g}{\partial x_1^2}\right)\frac{1}{3N}\int_0^\infty\langle\vec{J}_c(t)\cdot\vec{J}_c(0)\rangle\,dt \tag{3.54}$$

where $\vec{J}_c(t) = x_2\vec{J}_1(t) - x_1\vec{J}_2(t)$ is the fluctuating interdiffusion current. Note that for an <u>ideal</u> mixture, $\partial^2 g/\partial x_1^2 = (x_1x_2)^{-1}$; most alloys of simple metals are fairly close to ideality. Finally, by making the same assumption leading to the Nernst-Einstein relation (3.37), we arrive at the approximate relation :

$$D = x_2 D_1 + x_1 D_2$$

which is fairly well verified for mixtures of neutral fluids [36], but remains to be checked for alloys.

3.5. Charge density fluctuations.

We now examine the case of a binary ionic fluid containing ions of opposite charge. The important dynamical variables are now the Fourier components of the charge density (2.19) and of the associated electric current :

$$\vec{J}_{kZ} = Z_1\vec{J}_{k1}(t) + Z_2\vec{J}_{k2}(t) \tag{3.55}$$

The corresponding correlation functions are :

$$F_{zz}(k,t) = \frac{1}{N}\langle \rho_{\vec{k}z}(t)\,\rho^{*}_{\vec{k}z}(0)\rangle \tag{3.56}$$

and the longitudinal and tranverse charge current correlation functions $C^{L}_{zz}(k,t)$ and $C^{T}_{zz}(k,t)$ defined as in eqs.(3.44).

The response of the fluid to a time-dependent external potential is measured by the dynamic (frequency-dependent) generalization of the static charge response function introduced in eq.(2.31) ; by virtue of the fluctuation-dissipation theorem this complex dynamic response function is entirely determined by the equilibrium charge fluctuation spectrum, i.e. :

$$\chi''_{zz}(k,\omega) = -\frac{n\omega}{k_B T} S_{zz}(k,\omega) \tag{3.57}$$

while the real part follows from the standard Kramers-Kronig relation :

$$\chi'_{zz}(k,\omega) = P\int_{-\infty}^{+\infty} \frac{\omega'}{\omega'-\omega}\chi''_{z}(k,\omega')\,d\omega' \tag{3.58}$$

The longitudinal complex dielectric function is determined by the dynamical generalization of eq.(2.34) :

$$\frac{1}{\varepsilon(k,\omega)} = 1 + \frac{4\pi e^2}{k^2}\chi_{zz}(k,\omega) \tag{3.59}$$

The function χ_{zz} and ε^{-1} measure the linear response of the plasma to an external field. As was already pointed out for the static case, this external field polarizes the fluid and creates a local internal electric field which is the super-position of the external field (or electric displacement field) and of the field due to the induced charge density ; this local (or screened) electric field is of course the field experienced by the particles ; the response of the fluid to the local electric field is characterized by the screened response function $\chi^{s}_{zz}(k,\omega)$ which is related to the dielectric function by (cf. eq.(2.40)) :

$$\varepsilon(k,\omega) = 1 - \frac{4\pi e^2}{k^2}\chi^{s}_{zz}(k,\omega) \tag{3.60}$$

The electrical conductivity tensor reelates the Fourier components of the induced electrical current to the Fourier components of the local electric field :

$$\begin{aligned} \vec{J}_z(\vec{k},t) &= \int_0^t \overleftrightarrow{\sigma}(\vec{k},t-t')\cdot\vec{E}(\vec{k},t') \\ \tilde{\vec{J}}_z(\vec{k},\omega) &= \overleftrightarrow{\tilde{\sigma}}(\vec{k},\omega)\cdot\tilde{\vec{E}}(\vec{k},\omega) \end{aligned} \tag{3.61}$$

The decomposition of $\vec{E}$ into its logitudinal and transverse parts leads to a similar distinction between longitudinal and transverse conductivities σ^{L} and σ^{T} . The former is directly related to the (longitudinal) dielectric function via the familiar expression :

$$\varepsilon(k,\omega) = 1 + \frac{4\pi i}{\omega}\sigma^{L}(k,\omega) \tag{3.62}$$

In the long wavelength limit, spatial isotropy imposes that longitudinal and transverse conductivities become equal :

$$\sigma^{L}(0,\omega) = \sigma^{T}(0,\omega) \equiv \sigma(\omega) \tag{3.63}$$

and in particular comparison of eqs.(3.60) and (3.62) shows that the static conductivity is given by :

$$\sigma = -e^2 \lim_{\omega\to 0}\,\omega\left[\lim_{k\to 0}\frac{1}{k^2}\chi^{s\,''}_{zz}(k,\omega)\right] \tag{3.64}$$

Note that $\sigma(\omega)$ is <u>not</u> directly related to the k→0 limit of the charge density fluctuation spectrum, (see eq.(3.57)) or, equivalently, of the longitudinal current fluctuation spectrum (cf. eq.(3.45)!), but rather to the corresponding spectrum of the <u>transverse</u> current correlation function, a fact intimately related to the k→0 singularity of the Coulomb potential [37,31, 12].

To obtain the k,ω→0 limit of the charge fluctuation spectrum, we proceed as in section 3.4 for the case of the concentration fluctuations. The continuity eq.(3.40) reads (with z =ω) here :

$$-i\omega\tilde{\rho}_z(\vec{k},\omega) = \rho_z(\vec{k},t=0) + i\vec{k}\cdot\tilde{\vec{J}}_z(\vec{k},\omega) \tag{3.65}$$

while Poisson's equation is written in the form :

$$-i\vec{k}\cdot\tilde{\vec{E}}(\vec{k},\omega) = 4\pi\tilde{\rho}_z(\vec{k},\omega) \tag{3.66}$$

These two equations are combined with the longitudinal projection of Ohm's law (3.61), yielding :

$$\tilde{\rho}_z(\vec{k},\omega) = \frac{\rho_z(\vec{k},t=0)}{-i\omega + 4\pi\sigma^{L}(\vec{k},\omega)} \tag{3.67}$$

Upon multiplication of eq.(3.67) by $\rho_z^*(\vec{k},0)$ and statistical averaging we arrive at :

$$\tilde{F}_{zz}(k,\omega) = \frac{S_{zz}(k)}{-i\omega + 4\pi\sigma^L(k,\omega)} \tag{3.68}$$

which shows that $\sigma^L(k,\omega)$ is the memory function for the charge density correlation function. Taking the limit k→0

$$\lim_{k\to 0} \frac{\tilde{F}_{zz}(k,\omega)}{S_{zz}(k)} = \frac{1}{-i\omega + 4\pi\sigma(\omega)} \tag{3.69}$$

The corresponding spectrum (3.12) takes the form :

$$\lim_{k\to 0} \frac{S_{zz}(k,\omega)}{S_{zz}(k)} = \frac{1}{\pi} \frac{4\pi\sigma'(\omega)}{[\omega - 4\pi\sigma''(\omega)]^2 + [4\pi\sigma'(\omega)]^2} \tag{3.70}$$

which assumes the following low frequency limit ($\sigma'(\omega) \to \sigma$; $\sigma''(\omega) \to 0$) :

$$S_{zz}(k,\omega) = \frac{1}{\pi} \frac{4\pi\sigma k^2/(k_D^2\,\overline{Z^2})}{\omega^2 + (4\pi\sigma)^2} \quad ; k,\omega \to 0 \tag{3.71}$$

a result to be contrasted with the hydrodynamic limit (3.52) for $S_{cc}(k,\omega)$: whereas the width of the concentration fluctuation spectrum vanishes with k, it stays finite for the charge fluctuation spectrum in the limit k→ 0.
The long wavelength high frequency dielectric behaviour, on the other hand, follows directly from the sum rule (3.36) and the high frequency expansion (3.15) which leads immediately to :

$$\sigma(\omega) = \frac{i\omega_p^2}{4\pi\omega}\left[1 + o\left(\frac{1}{\omega^2}\right)\right]$$

Using (3.62) we find :

$$\varepsilon(0,\omega) = 1 - \frac{\omega_p^2}{\omega^2} + o\left(\frac{1}{\omega^4}\right) \tag{3.72}$$

which indicates the possible existence of a high frequency "optic mode" in ionic liquids , similar to the optic mode observed in ionic crystals, or to the familiar plasma oscillations in plasmas.

To conclude this section we stress once more the fact that the long range of the Coulomb interaction leads to different k→0 limits of the longitudinal and transverse electric current correlation functions. This is exemplified by the different k→0 limits of the longitudinal and transverse frequency moments (3.14). Defining the characteristic longitudinal and transverse "optic mode" frequencies via :

$$\omega_{L,T}^2(k) = \frac{\Omega_{zz}^{(2)L,T}(k)}{\Omega_{zz}^{(0)L,T}(k)}$$

a straighforward calculation [6] leads to the result :

$$\lim_{k\to 0}\left[\omega_L^2(k) - \omega_T^2(k)\right] = \omega_p^2 \tag{3.73}$$

which generalizes the Lyddane-Sachs-Teller sum rule for ionic crystals.

3.6. Mass density fluctuations.

Another, physically important, linear combination of the partial densities is the mass density :

$$\rho_{kM}(t) = \sum_\alpha m_\alpha \rho_{k\alpha}(t) \tag{3.74}$$

The corresponding mass density correlation function is :

$$\begin{aligned} F_{MM}(k,t) &= \frac{1}{N}\left\langle \rho_{kM}(t)\,\rho_{kM}^*(0)\right\rangle \\ &= \sum_\alpha\sum_\beta m_\alpha m_\beta (x_\alpha x_\beta)^{1/2} F_{\alpha\beta}(k,t) \end{aligned} \tag{3.75}$$

The hydrodynamic limit of the associated spectrum can be derived from the Navier-Stokes equations and lead in particular, to the following Kubo limit [38] :

$$\lim_{\omega\to 0}\lim_{k\to 0} \frac{\omega^4}{k^4} S_{MM}(k,\omega) = 2k_B T\left(\frac{4}{3}\eta + \zeta\right) \tag{3.76}$$

where η and ζ are the shear and bulk viscosities, respectively. The result (3.76) is the same for charged and for neutral fluids.

The coupling between mass and concentration fluctuations (in the case of binary alloys), or between mass and charge fluctuations (for ionic liquids), is characterized by the cross correlation function $F_{MC}(k,t)$ or $F_{MZ}(k,t)$.

4. SELECTED APPLICATIONS (PART 1).

In this and the following chapter we briefly review some salient features of a few typical Coulombic fluids in the light of the more general framework introduced in the preceding lectures. The present chapter will be mostly devoted to the "one component plasma" (OCP) model and some of its extensions and applications ; the last chapter will be mostly devoted to two-component ionic liquids. These lectures should only be considered as a brief introductory guide to a few aspects of this rich variety of charged fluids, and the reader should consult the (incomplete) list of references for more details.

4.1. The one component plasma.

The OCP model has been defined in section 1.3. Its essential virtue is its simplicity, but the model does exhibit some of the essential characteristics of Coulombic fluids, despite some very unphysical features associated with the rigid uniform background ; in particular mass and charge density fluctuations coincide in the OCP, so that the electrical conductivity is zero, due to total momentum conservation. The model is thoroughly reviewed in reference [19] which contains, in particular, a rather complete list of original references.

The OCP thermodynamics and static structure are very accurately known from computer simulations [19] ; these static properties are accurately reproduced by HNC theory and its extensions. The isothermal compressibility goes negative for $\Gamma \gtrsim 3$, without any incidence on thermodynamic stability, due the local electric field fluctuations which inhibit large scale (small k) density fluctuations [14]. Short range order (i.e. an oscillatory g(r)) appears for $\Gamma > 2$. In the strong coupling limit ($\Gamma \gg 1$) the excess internal energy is within a few percent of the simple ion-sphere result :

$$\frac{U^{ex}}{Nk_BT} = -\frac{9}{10}\,\Gamma$$

which represents in fact an exact lower bound to the energy. The OCP crystallizes into a BCC lattice at $\Gamma \simeq 170$ [39].

The dynamical properties of the OCP have been extensively studied by "molecular dynamics" simulations [40,19]. The most striking features are the following :

a) The velocity ACF exhibits marked oscillations at roughly the plasma frequency ω_p, for sufficiently strong couplings ($\Gamma > 10$) ; these oscillations are more and more pronounced and long-lived as Γ increases ; they are a clear manifestation of a strong coupling of the single particle motion to the collective charge density fluctuations [41].

b) The shear viscosity first decreases with increasing coupling, goes through a minimum at $\Gamma \simeq 20$ and then increases gradually until crystallization [42].

c) Conservation of total momentum implies that the high frequency plasmon mode is undamped in the $k \to 0$ limit. This mode exhibits negative dispersion (i.e. $d\omega / dk < 0$) for $\Gamma \gtrsim 10$. The simulation results are surprisingly well reproduced by a simple memory function analysis of the density ACF F(k,t) ; from equations (2.23) and (3.42) :

$$\tilde{F}(k,z) = \frac{S(k)}{-iz + \tilde{M}_1(k,z)} \tag{4.1}$$

Comparing the high frequency expansions (3.15) of $\tilde{F}$ and $\tilde{M}_1$ we find that

$$M_1(k,t=0) = \frac{\Omega^{(2)}(k)}{\Omega^{(0)}(k)} = \frac{v_0^2 k^2}{S(k)} \equiv \omega_{0\ell}^2(k) \tag{4.2}$$

where $v_0 = (k_B T/m)^{1/2}$ is the thermal velocity. The first order memory function M_1 can itself be expressed in terms of a second order memory function M_2 via equation (3.23). For the later we make a single relaxation time approximation ;

$$M_2(k,t) = M_2(k,t=0)\exp\{-t/\tau(k)\}$$
$$\tilde{M}_2(k,z) = \frac{M_2(k,t=0)}{-iz + 1/\tau(k)} \tag{4.3}$$

The initial value of M_2 is again easily derived from the high frequency expansion (3.15) with the result :

$$M_2(k,t=0) = \omega_{1\ell}^2(k) - \omega_{0\ell}^2(k) \tag{4.4}$$

where :

$$\omega_{1\ell}^{2}(k)=\frac{\Omega^{(4)}(k)}{\Omega^{(2)}(k)}=\frac{1}{v_0^2k^2}\,\Omega^{(4)}(k) \qquad (4.5)$$

This static quantity is expressible in terms of the pair disbritution function [40] :

$$\omega_{1\ell}^{2}(k)=\omega_p^2\left[1+\frac{3v_0^2k^2}{\omega_p^2}+2\int_0^\infty\frac{dr}{r}\bigl(g(r)-1\bigr)j_2(kr)\right] \qquad (4.6)$$

where j_2 denotes the second order spherical Bessel function.

Inserting equations (4.2-4.4) into equation (4.1), and taking the real part, we obtain the following expression for the dynamical structure factor :

$$\begin{aligned}S(k,\omega)&=\frac{1}{\pi}\tilde{F}'(k,\omega)\\&=\frac{1}{\pi}\frac{\tau(k)v_0^2k^2\left[\omega_{1\ell}^2(k)-\omega_{0\ell}^2(k)\right]}{\left\{\omega\tau(k)\left[\omega^2-\omega_{1\ell}^2(k)\right]\right\}^2+\left\{\omega^2-\omega_{0\ell}^2(k)\right\}^2}\end{aligned} \qquad (4.7)$$

Following Lovesey [43] we construct the unknown relaxation time τ (k) from the two characteristic frequencies $\omega_{0\ell}$(k) and $\omega_{1\ell}$ (k), by choosing that combination which ensures that for large k (wavelengths much shorter than the interparticle spacing), $S(k,\omega=0)$ goes over correctly to its free particle limit :

$$\lim_{k\to\infty} S(k,0)=\left[2\pi v_0^2k^2\right]^{-1/2}$$

This leads immediately to :

$$\tau_\ell(k)=\left\{\frac{4}{\pi}\left[\omega_{1\ell}^2(k)-\omega_{0\ell}^2(k)\right]\right\}^{-1/2} \qquad (4.8)$$

The dielectric function is then derived from $S(k,\omega)$ via equations (3.57-3.59). The plasmon dispersion curve $\omega=\omega(k)$ is determined by the equation :

$$\varepsilon\left(k,\omega(k)\right)=0 \qquad (4.9)$$

For small wave-numbers the damping of the plasmon mode is negligibly small and $\omega(k)$ is practically determined by the position of the plasmon peak in the charge fluctuation spectrum $S(k,\omega)$. The dispersion relation reads :

$$\omega(k)=\omega_p\left[1+\gamma\frac{k^2}{k_D^2}+O(k^4)\right] \qquad (4.10)$$

with $\gamma=3/2+2(U^{ex}/Nk_BT)/15$. Since the excess internal energy behaves essentially as -0.9Γ , γ changes sign for $\Gamma\simeq 13$, in agreement with the negative dispersion observed in the computer simulations [40] .

4.2. Liquid metals

The OCP model is a reasonable starting point for the description of very dense coulombic matter occurring in extreme astrophysical situations. For instance in a white dwarf star, densities are of the order of 10^6 - 10^8 gr/cm^3 and temperatures are typically 10^7 - 10^8 K. Under such conditions matter is metallic and made up of fully stripped ions (e.g. C^{6+} nuclei) and highly degenerate electrons (the Fermi temperature $T_F \simeq 10^{10}$ K). The electron screening length (1.9) far exceeds the inter-ionic spacing, so that the electron gas can, to a good approximation, be looked upon as providing a rigid, uniform background in which the classical positive ions move. Under typical white dwarf conditions the ionic coupling constant is large ($\Gamma > 10$) and during the cooling process, the ionic plasma will finally cristallize ("diamonds" in the sky [44]).

When the density decreases (and hence the parameter r_s increases), the electron gas is increasingly polarized by the ionic charge distribution and electron screening effects must be taken into account. If the screening remains moderate ($r_s < 1$), these effects can be treated by thermodynamic perturbation theory [45] . Such calculations show that the thermodynamic properties and the pair structure are surprisingly little affected by electron screening, as long as $\lambda_{TF} \gtrsim a$. The OCP is hence a reasonable model for metallic hydrogen under physical conditions occurring in the interior of Jupiter or Saturn.

When the density is further decreased, some of the electrons recombine with the muclei to form ions having a finite core ($r_c \simeq 1$ Å in the alkali) ; the nearly free conduction electrons interact with these ions via relatively weak pseudopententials, which can be treated by perturbation theory. The OCP has been used as a successful starting point for the description of simple liquid metals [46] . The success of this approach is linked to two simple observations. Under triple point conditions the Coulomb coupling parameter Γ for the liquid alkali, as determined from their density and temperature, is typically of the order of 180-200, strikingly close to the OCP melting conditons ($\Gamma \simeq 170$). By a simple density scaling of the wavenumbers, the static structure factors of the alkali just above melting are practically undistinguishable, and are surprisingly well represented by the OCP structure factor taken under the same temperature-density conditions [35,47] ; the only disagreement is at long wavelengths ($k \rightarrow 0$) where the ionic structure factor of the alkali tends towards the isothermal compressibility (cf. eq. (2.45)), while the OCP structure factor vanishes as k^2 (cf. eq. (2.42)).

This defect can be overcome by accounting for electron polarization effects through perturbation theory [46] . A fluctuation in the ion density induces a fluctuation in the electron density ; within the linear response relation (2.29) this reads :

$$\begin{aligned} \delta\rho_e(k) &= \chi_{ee}(k)\,\phi_e(k) \\ &= \chi_{ee}(k)\,\hat{v}_{ei}(k)\,\delta\rho_i(k) \end{aligned} \tag{4.11}$$

where $\hat{v}_{ei}(k)$ is the (weak) electron-ion potential. The Fourier components of the <u>effective</u> potential acting on the ions due to the fluctuation $\delta\rho_i(k)$ is the sum of a direct term and of an indirect electron polarization term :

$$\begin{aligned} \hat{v}_{eff}(k)\,\delta\rho_i(k) &= \hat{v}_{ii}(k)\,\delta\rho_i(k) + \hat{v}_{ei}(k)\,\delta\rho_e(k) \\ &= \left\{\hat{v}_{ii}(k) + \chi_{ee}(k)\left[\hat{v}_{ei}(k)\right]^2\right\}\delta\rho_i(k) \end{aligned} \tag{4.12}$$

Consequently :

$$\begin{aligned} \hat{v}_{eff}(k) &= \hat{v}_{ii}(k) + \hat{w}(k) \\ \hat{w}(k) &= \frac{\left[\hat{v}_{ei}(k)\right]^2}{4\pi e^2/k^2}\left[\frac{1}{\varepsilon_e(k)} - 1\right] \end{aligned} \tag{4.13}$$

where $\varepsilon_e(k)$ is the dielectric constant of the degenerate Fermi gas of interacting conduction electrons, which is related to the static response function $\chi_{ee}(k)$ by equation (2.34). In equation (4.13), $\hat{v}_{ii}(k)$ is the direct ion-ion interaction ; this reduces to the Coulomb repulsion $4\pi Z^2e^2/k^2$ which is sufficient to prevent the ion cores from touching ; $\hat{w}(k)$ is the electron-induced indirect ion-ion interaction which will be treated as a perturbation. The ion-electron pseudopotential $v_{ei}(r)$ can be approximated with reasonable accuracy by the Ashcroft empty-core model [48] :

$$\begin{aligned} v_{ei}(r) &= 0 \quad ; r < r_c \\ &= -\frac{Ze^2}{r} \quad ; r > r_c \\ \hat{v}_{ei}(k) &= -\frac{4\pi Ze^2}{k^2}\cos(kr_c) \end{aligned} \tag{4.14}$$

where the core radius is fitted to solid state date.

The ionic structure factor is finally calculated by a generalized RPA [45] . If $S_0(k)$, $\hat{c}_0(k)$ and $S(k)$, $\hat{c}(k)$ are the structure factor and the direct correlation function for a reference system (in the present case the OCP) and of the system of interest, these quantities are related by the exact expression (which follows trivially from equation (2.16b)

$$S(k) = \frac{S_0(k)}{1 - \left[\hat{c}(k) - \hat{c}_0(k)\right]S_0(k)} \tag{4.15}$$

The RPA (2.55a) is now applied to the <u>difference</u> $\hat{c}(k) - \hat{c}_0(k)$, resulting in :

$$S(k) = \frac{S_0(k)}{1 + \beta\,\hat{w}(k)} \tag{4.16}$$

The small k limit of the resulting structure factor is obtained from eqs. (4.13), (4.14) and the limiting forms :

$$\varepsilon_e(k) = 1 + \frac{k_e^2}{k^2} \qquad (4.17a)$$

$$S_o(k) = \frac{k^2}{k_D^2}\left[1 + \frac{k^2}{k_S^2}\right]^{-1} \qquad (4.17b)$$

where k_e is the inverse screening length of the electron gas, k_s is the inverse screening length of the OCP, given by eq.(2.51), and $k_D = (4\pi n Z^2 e^2/k_B T)^{1}$ is the Debye wave number. The resulting expression for the isothermal compressibility reads :

$$n_i k_B T \chi_T = \lim_{k\to 0} S(k) = \left[\frac{k_D^2}{k_e^2} + \frac{k_D^2}{k_S^2} + k_D^2 r_c^2\right] \qquad (4.18)$$

which leads to values for liquid alkali in satisfactory agreement with experiment (typically $n_i k_B T \chi_T \simeq 0.02$) [46].

Historically the point of view of considering a simple liquid metal as a perturbed OCP goes back to Bohm and Staver [49] who identified sound waves in liquid metals with screened plasmons. The screened ionic plasma frequency yields an acoustic phonon-like dispersion :

$$\omega(k) = \left[\frac{\omega_p^2}{\varepsilon_e(k)}\right]^{1/2} = \left[\frac{4\pi n_i Z^2 e^2}{m_i \varepsilon_e(k)}\right]^{1/2} \underset{k\to 0}{=} c\,k$$

where, in view of the limit (4.17a), the speed of sound is given by :

$$c = \left[\frac{4\pi n_i Z^2 e^2}{k_e^2}\right]^{1/2} = \left[\frac{1}{3} Z \frac{m_e}{m_i}\right]^{1/2} v_F$$

v_F is the Fermi velocity and the inverse screening length k_e is taken to be that of an ideal Fermi gas.

4.3. Charged colloidal dispersions.

Macroionic solutions contain large ions, carrying up to several hundred elementary charges, and small counterions which form essentially a screening cloud around the much larger macroions. Typical examples are polyelectrolytes, micelles and colloids. In this section we briefly examine the latter which have been the object of intense experimental investigations in recent years.

Colloids cover a wide range of colloidal particles, containing a large number of ionizable sites, dispersed in a solvent (generally water). Typical examples are organic colloids, like certain globular viruses or polymer microspheres (e.g. polystyrene balls) or inorganic crystallites, like the Ag I sol or certain suspended silica. Colloidal particles have sizes ranging between 10^2 and 10^4 Å and acquire a large electric charge in solution. Because of the large size of the colloidal particles, interfacial phenomena play a dominant role. The main characteristic of this interface is its electrical polarization : the charged colloidal particles are surrounded by a cloud of counterions, thus giving rise to an electric double layer having a spatial extension determined by the Debye screening length (λ_D is typically of the order of 10^3 - 10^4 Å in colloids, depending on the counterion concentration). The colloidal particles interact hence via screened electrostatic repulsion. It is this repulsion which stabilizes the suspension and prevents agglomeration. The addition of small amounts of electrolyte to the suspension results in a decrease of the screening length, and hence of the Coulomb repulsion, and can provoke coagulation (or flocculation) of the suspension. In this section we restrict ourselves to monodisperse colloids, made up of spherical particles of practically identical diameters ; suspensions of polystyrene balls come very close to such an ideal situation. Light or small angle neutron scattering experiments of the static structure factor of such colloids have revealed a considerable amount of liquid-like short range order [50] and in many situations such suspensions have been observed to solidify into colloidal crystals [51]. This crystallization is a Coulomb correlation effect, because the particles are observed to occupy regular lattice sites long before they are closely packed.

In the immediate vicinity of a large colloidal particle its curvature can be neglected in first approximation and the double layer can be considered as planar. The electric potential in the double layer and the charge profile of the counterions can be determined from the one-dimensional Poisson-Boltzmann equation (Gouy-Chapman theory [52]). If x denotes the coordinate perpendicular to the surface, $\Phi(x)$ the electrostatic potential and $\rho(x)$ the charge profile, the Poisson eq.(2.56b) takes here the form :

$$\frac{d^2\Phi(x)}{dx^2} = -\frac{4\pi e^2}{\varepsilon}\rho(x) \qquad (4.19)$$

where ε is the dielectric constant of the medium. Assuming that the positive and negative counterions have the same absolute valence Z, the density profile is related to the potential by :

$$\begin{aligned}\rho(x) &= Z\left[\rho_+(x) - \rho_-(x)\right] \\ &= Z\,n\,\sinh\left[Ze\,\Phi(x)/k_B T\right] \qquad (4.20)\end{aligned}$$

Contrarily to their three-dimensional counterpart, the set of equations (4.19-20) can be solved analytically without linearization [52] . For large distances x the potential decays exponentially, and the screening length is the Debye length :

$$\lambda_D = \left[4\pi n Z^2 e^2/(\varepsilon k_B T)\right]^{-1/2} \qquad (4.21)$$

The mutual interaction of two inter-penetrating double layers (and hence of two colloidal particles surrounded by their clouds of conterions) is then calculated to be [52] :

$$v(r) = \pi\,\varepsilon\,\sigma^2\,\psi_0^2\,\exp\{-(r-\sigma)/\lambda_D\}/r \qquad (4.22)$$

where ψ_0 is the potential at the surface of the colloidal particles, and σ their diameter. The potential (4.22) is of the screened Coulomb form, as expected. The simplest model of a colloid is consequently a collection of hard spheres interacting via the potential (4.22) ; the counterions appear only through the screening length λ_D and the solvent through the dielectric constant ; such semi-macroscopic assumptions are justified in view of the large size of the colloidal particles compared to that of the counterions and the solvent molecules. The MSA, introduced in section 2.5, has been solved analytically for that model [53]. However, since the MSA yields poor results for low packing fractions ($\eta = \pi n_c \sigma^3/6 \ll 1$, where n_c is the number of colloidal particles per unit volume), the physical diameter σ is increased to an effective diameter $\sigma' > \sigma$, which does not affect the structure (because of the strong Coulomb repulsion which prevents the particles from coming into contact) but strongly improves the accuracy of the MSA ; σ' is chosen such that $v(\sigma')$ remains large compared to $k_B T$ [54]. This procedure yields colloid structure factors in excellent agreement with experimental data [50].

Before closing this section it must be emphasized that the dynamics of colloidal particles in suspension, i.e. the dynamics of interacting Brownian particles, represents a fascinating subject of much current interest [55].

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