

# COULOMB SYSTEMS

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# Hoofdstuk 1

## Equilibrium properties

### 1.1 Introduction

Astrophysical estimates indicate that the greater part of matter in the universe consists of partly or completely ionized atoms and molecules. Hence, the customary emphasis in statistical physics on neutral fluids and solids testifies to a rather narrow “geocentric” point of view. This biased interest is even less understandable, if one is reminded of the importance of physical processes in charged-particle systems on earth, like gas discharges, electrolytes, fusion experiments etcetera. In the following an attempt will be made to convince the reader that statistical physics of charged-particle systems is not only a relevant, but also a quite interesting discipline.

In general the interaction between charged particles proceeds through the electromagnetic field. A statistical theory of a general charged-particle system (or a plasma, as it is often called) must deal with all intricacies of the electromagnetic interaction like retardation effects and relativistic corrections. Such a theory is necessarily rather complicated; as an important concept it makes use of “retarded distribution functions” [1]. Fortunately, a much simpler description is possible if the particles move relatively slowly. In that case both magnetic interactions and retardation effects can be neglected; the interaction between the particles is then given by the electrostatic Coulomb forces. The statistical theory for these Coulomb systems has made considerable progress in recent years. In particular, efforts have been concentrated on dense or “strongly coupled” Coulomb systems. In these systems the ratio of averaged potential (Coulomb) to thermal kinetic energy is of the order of 1 or higher. Earlier theories were confined to dilute systems where this ratio is much less than 1. Incidentally, the word “dense” must not be taken too literally. In fact, the ratio that was used in its definition clearly depends on both particle density and temperature. As we shall see presently, it is better to use the qualifications “hot dilute” as opposed to “cold dense” in typifying Coulomb systems.

Charged particles attract or repel each other depending on the sign of their charges. All Coulomb systems in nature contain charges of both signs. As these can form bound states under suitable circumstances a Coulomb system has to be described by a mixture of “free” charged particles and of composite particles, which can be either charged or neutral. For systems in equilibrium Saha-type equations

may be used to determine the fractions of “free” and bound particles in the system. As is well-known the bound states can not be described correctly without using quantum mechanics. Indeed, one can show that a purely classical statistical theory of Coulomb systems with (point) charges of opposite sign can not be formulated consistently, since the system is not stable. Hence, it seems that one is obliged to choose a quantummechanical description, if one wishes to understand the properties of Coulomb systems.

The picture described so far is not complete, however. As it turns out one can construct a model Coulomb system, which on the one hand is still realistic and on the other allows a classical statistical description. This model is called the *one-component plasma (OCP)*. It consists of a set of charged particles, with all charges equal, which move in an inert uniformly smeared background of opposite charge, such that the system as a whole is neutral. Since the particles can not form bound states in this model a classical description looks as being feasible. As we shall see in the next section, it has indeed been proved that the model can consistently be treated with the help of classical statistical mechanics. Moreover, it turns out that several systems in nature can, to a fair degree of approximation, be described by the OCP model. For instance, in the interior of white dwarf stars carbon nuclei move in an almost uniform sea of electrons. As a second example we mention liquid metals which can, to lowest order, be described as an OCP in a (polarizable) background of degenerate electrons.

The physical conditions that must be fulfilled by a Coulomb system in order to be treatable as an OCP can be formulated once a few parameters have been defined. In view of the examples just mentioned we will talk about the charged particles as ions, while the background will be assumed to be represented by an electron gas.

The ions, with charge  $e_i = Ze$ , are supposed to have a density  $n_i$ , so that the so-called *ion radius*  $a$ , defined through  $n_i^{-1} = (4\pi/3)a^3$ , is a measure of the average distance between neighbouring particles. In equilibrium the average distance of closest approach of the ions is given by the *Landau length*  $\lambda_L = \beta e_i^2 / (4\pi)$ , with  $\beta$  the inverse temperature. The ratio of these two length scales is the *plasma parameter*  $\Gamma = \lambda_L / a$ . Alternatively, one may write  $\Gamma = \beta e_i^2 / (4\pi a)$ , which shows that  $\Gamma$  is a measure for the ratio of the average Coulomb energy of a pair of neighbouring particles and the average kinetic energy per particle. Clearly,  $\Gamma$  is proportional to  $n^{1/3} T^{-1}$ . In hot dilute systems one has  $\Gamma \ll 1$ , whereas for a cold dense (or strongly coupled) OCP the plasma parameter is of the order of 1 or higher.

Turning to the electrons, we see that their density is  $n_e = Zn_i$ , since the system is neutral. Their average distance is thus  $a_e = Z^{-1/3}a$ . The thermal wavelength of the electrons is  $\lambda_{T,e} = h[\beta/(2\pi m_e)]^{1/2}$ , with  $m_e$  the electron mass. The electrons will be degenerate, if  $a_e/\lambda_{T,e} \ll 1$ . The ratio occurring here is by a factor of  $Z^{-1/3}(m_e/m_i)^{1/2}$  (which is of the order of 1/100 or less) smaller than the corresponding ratio for the ions. Hence, the electrons can be fully degenerate, whereas the ions are still completely classical. The electron gas remains without structure in the presence of the ions, if the average inter-electron distance  $a_e$  is much smaller than the Bohr radius  $a_0 = h^2/(\pi m_e e^2)$ . The ratio of these quantities is usually called  $r_s$ . The condition on the degeneracy of the electrons can be formulated in terms of this parameter as well, since one has  $a_e/\lambda_{T,e} = [r_s/(2\pi\Gamma)]^{1/2} Z^{5/6}$ .

Likewise, one may write the corresponding degeneracy parameter of the ions as  $a_i/\lambda_{T,i} = [r_s/(2\pi\Gamma)]^{1/2}(m_i/m_e)^{1/2}Z^{7/6}$ .

In conclusion we may state the conditions on the validity of the OCP model for a mixture of ions and electrons as follows:

$$r_s \ll 1 \quad , \quad \left(\frac{r_s}{2\pi\Gamma}\right)^{1/2} Z^{5/6} \ll 1 \quad , \quad \left(\frac{r_s}{2\pi\Gamma}\right)^{1/2} \left(\frac{m_i}{m_e}\right)^{1/2} Z^{7/6} \gg 1 \quad . \quad (1.1.1)$$

For the interior of a typical white dwarf star (with carbon ions) the plasma parameter  $\Gamma$  equals 17, as follows from its ion density  $n_i = 5 \times 10^{30} \text{ cm}^{-3}$  and its temperature  $T = 10^8 \text{ K}$  [2]. The other relevant parameters are in this case:

$$r_s = 0.004 \quad , \quad \left(\frac{r_s}{2\pi\Gamma}\right)^{1/2} Z^{5/6} = 0.03 \quad , \quad \left(\frac{r_s}{2\pi\Gamma}\right)^{1/2} \left(\frac{m_i}{m_e}\right)^{1/2} Z^{7/6} = 7 \quad . \quad (1.1.2)$$

Clearly, all conditions on the validity of the OCP are fulfilled.

For not too high plasma parameter the particles in the OCP model move in an unordered way, as in a fluid. If  $\Gamma$  increases above the value  $\Gamma_c = 178$ , however, the particles have been found to crystallize in a body-centered cubic structure, a so-called Wigner lattice. The freezing transition is of first-order, with a non-vanishing latent heat.

In the following we shall review some recent work on the statistical properties of the one-component plasma model in the fluid phase. Further general information can be found in review papers that have appeared lately [2] – [5].

## 1.2 Stability and equivalence of ensembles

The Hamiltonian of a one-component plasma (OCP) consisting of  $N$  particles with charge  $e$  and mass  $m$ , which move in a neutralizing background with charge density  $-ne$ , reads:

$$\begin{aligned} H_N &= \sum_{i=1}^N \frac{p_i^2}{2m} + \frac{1}{2} \sum'_{i,j=1}^N \frac{e^2}{4\pi |\mathbf{r}_i - \mathbf{r}_j|} \\ &\quad - n_B \sum_{i=1}^N \int_V d\mathbf{r} \frac{e^2}{4\pi |\mathbf{r} - \mathbf{r}_i|} + \frac{1}{2} n_B^2 \int_V d\mathbf{r} \int_V d\mathbf{r}' \frac{e^2}{4\pi |\mathbf{r} - \mathbf{r}'|} \\ &\equiv T_N(\mathbf{p}^N) + \Phi_N(\mathbf{r}^N; n_B, V) \quad , \end{aligned} \quad (1.2.1)$$

where the prime at the summation symbol indicates that the terms with  $i = j$  have to be excluded. The system is neutral if the density  $n_B$  of the background equals the density  $n = N/V$  of the particles. Owing to the presence of the background terms the Hamiltonian depends explicitly on  $n_B$  and on the volume  $V$  of the plasma. This dependence, which is absent in the usual Hamiltonians that describe systems of neutral particles, leads to some unusual properties of the OCP, as we shall see in the following.

Starting from the Hamiltonian (1.2.1) we can determine the thermodynamical properties of the plasma in the usual way, by choosing an ensemble, writing down

the partition function and determining its form in the thermodynamic limit, which corresponds to  $N \rightarrow \infty$  and  $V \rightarrow \infty$  with fixed ratio  $n$ . For a system of neutral particles precise statements on the existence of the thermodynamic limit and on the equivalence of the well-known equilibrium ensembles are available in the literature. In fact, for a classical system of neutral particles interacting through a pair potential  $\varphi(r)$  it has been proved (see [6]) that the following conditions on  $\varphi$  are sufficient to ensure that the well-known ensembles (canonical, grand-canonical etc.) all yield consistent finite answers for the thermodynamic functions in the thermodynamic limit:

- a condition of *stability*, of the form  $\Phi_N(\mathbf{r}^N) \geq -AN$  for some  $A \geq 0$ , for all  $N$  and for all positions  $\mathbf{r}^N$  of the  $N$  particles within  $V$ ;
- a condition of so-called “*weak tempering*” of the pair potential, of the form  $\varphi(r) \leq B/r^{3+\varepsilon}$  for some  $B > 0$  and  $\varepsilon > 0$ , and for all  $r$  that are larger than some minimal value  $r_{min}$ .

Neither of the two conditions is fulfilled trivially by the Coulomb system with Hamiltonian (1.2.1). (The second condition can not even be checked as such, since  $\Phi_N$  is not a sum of pair potential terms.) A general Coulomb system in which particles of opposite charge are present behaves even worse in this respect. In fact, for such a general Coulomb system the energy may decrease indefinitely if the charges coalesce: such a Coulomb system will collapse. In nature this collapse does not occur, however: a gas of ionized atomic hydrogen is stable, since neutral hydrogen atoms are formed. Clearly a quantummechanical description is essential here. Indeed, it has been proved ([7], [8]) that a quantum Coulomb system with charges of opposite sign is stable, if at least one of the species of particles consists of fermions: our world would not exist if electrons were bosons.

A classical Coulomb system with charges of opposite sign is thus unstable. For a classical system with charges of one sign and with a neutralizing background the situation is quite different: here the proof of stability has been given (see [9]). This fact has been crucial in confining ourselves to the OCP, as we wish to stay within a classical framework.

As to the second condition, the Coulomb potential itself does not satisfy a weak tempering condition: it is essentially a long-range potential. However, it has turned out that for a general Coulomb system a weaker condition (contained in the so-called “cheese theorem”, see [10]) can be proved, which is already sufficient to guarantee the conclusions of the theorem stated above. The proof makes use of the screening phenomenon in a plasma. A similar result has been derived for the OCP [9].

The situation for the OCP as to the validity of the thermodynamic limit and the consistency of the various ensembles is thus rather comfortable. More precisely, the following statements have been established for the OCP [9]:

- the use of the canonical ensemble, with  $n_B = n$  leads to finite results in the thermodynamic limit;
- the use of the grand-canonical ensemble leads to finite results as well, if the density  $n_B$  is kept constant for all  $N$  (so that in general  $N/V$  will differ from



$n_B$ ); on the other hand, if  $n_B$  is chosen to be equal to  $N/V$  for each  $N$  separately the thermodynamic limit does *not* exist;

- the results of the grand-canonical ensemble agree with those of the canonical ensemble only if the thermodynamic potential  $\mu$  is chosen in accordance with the values of  $n_B$  and of the temperature  $T$ .

Finally, we remark that a rigorous proof of the existence of the thermodynamic limit for the equilibrium distribution functions has only been given for special cases up to now (see [5]).

### 1.3 Equation of state

For the canonical ensemble, with  $n_B = n$ , the partition function is:

$$Z_N = Z_N^{id} Q_N \quad , \quad (1.3.1)$$

with the dimensionless ideal-gas partition function  $Z_N^{id} = V^N (2\pi m / \beta h^2)^{3N/2} / N!$  and the dimensionless configurational partition function:

$$Q_N = \int_V \frac{d\mathbf{r}^N}{V^N} e^{-\beta \Phi_N(\mathbf{r}^N; n, V)} \quad . \quad (1.3.2)$$

The Coulomb potential is a homogeneous function of the particle positions. As a consequence the configurational partition function can be brought in a simpler form by a rescaling of the lengths. If all position vectors are rescaled by writing  $\mathbf{r} = a\tilde{\mathbf{r}}$  the potential energy  $\Phi_N$  becomes:

$$\begin{aligned} \Phi_N &= \frac{1}{2a} \sum'_{i,j=1}^N \frac{e^2}{4\pi |\tilde{\mathbf{r}}_i - \tilde{\mathbf{r}}_j|} - \frac{3}{4\pi a} \sum_{i=1}^N \int_{\tilde{V}} d\tilde{\mathbf{r}} \frac{e^2}{4\pi |\tilde{\mathbf{r}} - \tilde{\mathbf{r}}_i|} \\ &+ \frac{9}{32\pi^2 a} \int_{\tilde{V}} d\tilde{\mathbf{r}} \int_{\tilde{V}} d\tilde{\mathbf{r}}' \frac{e^2}{4\pi |\tilde{\mathbf{r}} - \tilde{\mathbf{r}}'|} \equiv \frac{e^2}{4\pi a} \tilde{\Phi}_N(\tilde{\mathbf{r}}^N) \quad , \end{aligned} \quad (1.3.3)$$

with the scaled volume  $\tilde{V} = 4\pi N/3$ . Hence  $Q_N$  can be written as:

$$Q_N = \frac{1}{\tilde{V}^N} \int_{\tilde{V}} d\tilde{\mathbf{r}}^N e^{-\Gamma \tilde{\Phi}_N(\tilde{\mathbf{r}}^N)} = Q_N(\Gamma) \quad , \quad (1.3.4)$$

with the plasma parameter  $\Gamma = \beta e^2 / (4\pi a)$ , as before. The configurational partition thus depends on the density  $n$  and the temperature  $T$  through the combination  $\beta n^{1/3}$ , which is proportional to  $\Gamma$ .

On account of (1.3.1) the dimensionless free energy per particle  $\beta f$  is the sum of an ideal-gas term  $\beta f^{id}$  and an “*excess*” term  $\beta f^{exc}$ . The latter is given by  $-\log Q_N(\Gamma)/N$ . In the thermodynamic limit it depends no longer on  $N$ , so that it becomes a function of  $\Gamma$  only. Writing this function as  $\psi(\Gamma)$  we have found for the free energy:

$$\begin{aligned} \beta f(n, \beta) &= \beta f^{id}(n, \beta) + \psi(\Gamma) = \\ &= \log n - \frac{3}{2} \log \left( \frac{2\pi m}{\beta h^2} \right) - 1 + \psi(\Gamma) \quad . \end{aligned} \quad (1.3.5)$$

(Of course only the excess term depends on  $\beta n^{1/3}$  or  $\Gamma$ , the ideal-gas term is a function of  $\beta n^{2/3}$ , as is well-known.)

Likewise the dimensionless internal energy per particle  $\beta u$ , the dimensionless thermodynamic pressure  $\beta p/n$ , the dimensionless specific heat per particle  $c_v/k_B$  and the dimensionless inverse isothermal compressibility  $\beta/(n\kappa_T)$  can be written as the sum of an ideal-gas term and an excess term:

$$\beta u = \frac{3}{2} + \Gamma \frac{\partial \psi}{\partial \Gamma} \quad , \quad (1.3.6)$$

$$\frac{\beta p}{n} = 1 + \frac{1}{3} \Gamma \frac{\partial \psi}{\partial \Gamma} \quad , \quad (1.3.7)$$

$$\frac{c_v}{k_B} = \frac{3}{2} + \Gamma \frac{\partial \psi}{\partial \Gamma} - \Gamma \frac{\partial}{\partial \Gamma} \left( \Gamma \frac{\partial \psi}{\partial \Gamma} \right) \quad , \quad (1.3.8)$$

$$\frac{\beta}{n\kappa_T} = 1 + \frac{1}{3} \Gamma \frac{\partial \psi}{\partial \Gamma} + \frac{1}{9} \Gamma \frac{\partial}{\partial \Gamma} \left( \Gamma \frac{\partial \psi}{\partial \Gamma} \right) \quad . \quad (1.3.9)$$

Owing to the scaling property of the potential  $u$  and  $p$  are closely connected:

$$\beta u = 3 \frac{\beta p}{n} - \frac{3}{2} \quad . \quad (1.3.10)$$

Similarly,  $c_v$  and  $1/\kappa_T$  are related:

$$\frac{c_v}{k_B} = -9 \frac{\beta}{n\kappa_T} + 4\beta u + \frac{9}{2} \quad . \quad (1.3.11)$$

Knowledge of the function  $\psi(\Gamma)$  suffices to calculate all thermodynamical properties of the OCP.

The thermodynamical pressure  $p$  is defined here in the usual way as  $n^2(\partial f/\partial n)_\beta$ . In differentiating with respect to  $n$  the background density that occurs in  $\Phi_N$  is differentiated as well. In view of this it is not at all clear that the thermodynamic pressure of the OCP has the same properties of convexity as the pressure of a system of neutral particles. Indeed, it turns out that the isothermal compressibility of the OCP can become negative. This fact does not lead to problems of stability, however, as is shown in detail in [11], [12].

The above results have been obtained with the use of the canonical ensemble. Let us consider now how one should proceed in the *grand-canonical ensemble*. The grand-canonical partition function reads:

$$Z_{gr}(\beta, \mu, n_B, V) = \sum_{N=0}^{\infty} \frac{e^{\beta \mu N}}{h^{3N} N!} \int d\mathbf{r}^N d\mathbf{p}^N e^{-\beta H_N(\mathbf{r}^N, \mathbf{p}^N; n_B, V)} \quad , \quad (1.3.12)$$

with fixed  $n_B$ . If  $N$  greatly differs from  $n_B V$  the electrostatic energy of the configuration becomes large and positive, so that the exponential function strongly suppresses the contributions of such  $N$ . This mechanism explains why the average particle density  $\langle N \rangle / V$  should be equal to the background density in the thermodynamic limit, as has been proved rigorously in [9]:

$$\lim_{(therm)} \frac{\langle N \rangle}{V} = y \left[ \frac{\partial}{\partial y} \frac{1}{V} \log Z_{gr} \right]_{\beta, n_B, V} = n_B \quad , \quad (1.3.13)$$

with the fugacity  $y = e^{\beta\mu}$ . Furthermore one can prove [9]:

$$\lim_{(therm)} \frac{1}{V} \log Z_{gr}(\beta, \mu, n_B, V) = n_B \beta [\mu - f^{can}(n_B, \beta)] \quad . \quad (1.3.14)$$

This identity can be understood by remarking that for large  $N$  the grand-canonical partition function is given approximately by the term with  $N = n_B V$  in (1.3.12), so that one gets for large  $N$  effectively  $Z_{gr} \simeq \exp(\beta\mu N) Z_N$  with  $N = n_B V$ . Taking the logarithm one arrives at (1.3.14). It should be remarked that at the right-hand side of (1.3.14) the free energy per particle (as found from the canonical ensemble) at the density  $n_B$  appears. It follows from (1.3.5) by replacing  $n$  by  $n_B$  and, correspondingly,  $\Gamma$  by  $\Gamma_B \equiv \beta e^2 / (4\pi a_B)$ , with  $a_B$  given by  $n_B^{-1} = 4\pi a_B^3 / 3$ .

The right-hand side of (1.3.14) depends – apart from  $T$  – on both the thermodynamical potential  $\mu$  (which is a free parameter up to now) and on the density  $n_B$ . Since these variables can be chosen arbitrarily, the expression between square brackets is not equal to  $n_B^{-1} p$  in general. Only if  $\mu$  is chosen in accordance with the value of  $n_B$  (at the given value of  $T$ ) does the right-hand side reduce to  $\beta p(\beta, \mu)$ , which is the usual result for a system of neutral particles. “Choosing  $\mu$  in accordance with  $n_B$ ” means that one adopts the value:

$$\mu = \mu^{can}(n_B, \beta) = \frac{\partial}{\partial n_B} [n_B f^{can}(n_B, \beta)]_{\beta} \quad . \quad (1.3.15)$$

As we have seen the grand-canonical ensemble for the OCP gives less freedom to the particle number  $N$  than one is accustomed to for systems of neutral particles. In fact, one easily proves formally that fluctuations in the particle number are strongly suppressed in the grand-canonical ensemble. Starting from the formula for the dispersion of the particle number:

$$\langle N^2 \rangle - \langle N \rangle^2 = y \frac{\partial}{\partial y} \langle N \rangle \quad , \quad (1.3.16)$$

with a differentiation at fixed values of  $\beta, V$  and also  $n_B$ , one gets in the thermodynamic limit:

$$\lim_{(therm)} \frac{1}{V} [\langle N^2 \rangle - \langle N \rangle^2] = \left[ y \frac{\partial}{\partial y} \lim_{(therm)} \frac{\langle N \rangle}{V} \right]_{\beta, n_B} \quad . \quad (1.3.17)$$

Substituting (1.3.13) one immediately gets 0 for the right-hand side, so that one arrives at the result:

$$\lim_{(therm)} \frac{\langle N^2 \rangle - \langle N \rangle^2}{V} = 0 \quad . \quad (1.3.18)$$

As a reminder we write the grand-canonical fluctuation formula of particle number for a system of neutral particles:

$$\lim_{(therm)} \frac{\langle N^2 \rangle - \langle N \rangle^2}{V} = \frac{n^2 \kappa_T}{\beta} \quad . \quad (1.3.19)$$

## 1.4 Distribution functions

In this section we shall define equilibrium distribution functions for the OCP and discuss a few of their properties. Furthermore, we shall derive the hierarchy equations that are satisfied by these functions.

The definition of the  $k$ -point equilibrium configurational distribution functions has the usual form:

$$n^k g^{(k)}(\mathbf{r}_1, \dots, \mathbf{r}_k) = \left\langle \sum'_{i_1, \dots, i_k} \delta(\mathbf{r}_1 - \mathbf{r}_{i_1}) \dots \delta(\mathbf{r}_k - \mathbf{r}_{i_k}) \right\rangle, \quad (1.4.1)$$

for  $k = 1, 2, \dots$ . The sum is extended over  $k$  independent particle labels  $i_1, \dots, i_k$ , with the prime indicating that all labels must be different. The angular brackets denote a canonical ensemble average. (The grand-canonical ensemble can be used as well; again one should be careful about the choice of compatible values of  $\mu$  and  $n_B$ , as before.) From the definition it follows immediately that  $g^{(1)}(\mathbf{r}_1) = 1$ . Inserting the definition of a canonical ensemble average one gets:

$$n^k g^{(k)}(\mathbf{r}_1, \dots, \mathbf{r}_k) = \frac{N!}{(N-k)!} \frac{1}{V^N Q_N} \int_V d\mathbf{r}^{N-k} e^{-\beta \Phi_N(\mathbf{r}^N; n, V)}, \quad (1.4.2)$$

or, for large  $N$ :

$$g^{(k)}(\mathbf{r}_1, \dots, \mathbf{r}_k) = \frac{1}{Q_N} \int_V \frac{d\mathbf{r}^{N-k}}{V^{N-k}} e^{-\beta \Phi_N(\mathbf{r}^N; n, V)}. \quad (1.4.3)$$

Performing a rescaling, as in (1.3.3), we obtain for the right-hand side:

$$\frac{1}{\tilde{V}^{N-k} Q_N} \int_{\tilde{V}} d\tilde{\mathbf{r}}^{N-k} e^{-\Gamma \tilde{\Phi}(\tilde{\mathbf{r}}^N)}. \quad (1.4.4)$$

Hence, in the thermodynamic limit the distribution functions  $g^{(k)}$  depend on the scaled position vectors  $\tilde{\mathbf{r}}_1, \dots, \tilde{\mathbf{r}}_k$  and on the plasma parameter  $\Gamma$  (the dependence on  $N$  or  $\tilde{V}$  drops out in the limit). On account of translation invariance the distribution functions depend only on the differences of the position vectors in the thermodynamic limit. Furthermore, rotation invariance ensures that the distribution functions are invariant if all position vectors are rotated simultaneously. In particular, this means that the pair distribution function depends only on the distance  $|\mathbf{r}_1 - \mathbf{r}_2|$  of the two positions.

The distribution functions satisfy a *hierarchy of equations* that is found by differentiating (1.4.2), with (1.2.1) inserted, with respect to  $\mathbf{r}_1$ :

$$\begin{aligned} n^k \nabla_{\mathbf{r}_1} g^{(k)}(\mathbf{r}_1, \dots, \mathbf{r}_k) &= \\ &= -\beta n^k g^{(k)}(\mathbf{r}_1, \dots, \mathbf{r}_k) \nabla_{\mathbf{r}_1} \left[ \sum_{j=2}^k \frac{e^2}{4\pi |\mathbf{r}_1 - \mathbf{r}_j|} - n \int_V d\mathbf{r} \frac{e^2}{4\pi |\mathbf{r}_1 - \mathbf{r}|} \right] \\ &\quad - \beta n^{k+1} \int_V d\mathbf{r}_{k+1} g^{(k+1)}(\mathbf{r}_1, \dots, \mathbf{r}_{k+1}) \nabla_{\mathbf{r}_1} \frac{e^2}{4\pi |\mathbf{r}_1 - \mathbf{r}_{k+1}|}, \end{aligned} \quad (1.4.5)$$

for  $k = 1, 2, \dots$ . To derive this hierarchy one should differentiate all terms in (1.2.1) that contain  $\mathbf{r}_1$ ; these are the particle-particle interaction term between particles  $i = 1$  and  $j = 2, \dots, k$  or  $j = k+1, \dots, N$ , and, furthermore, the particle-background interaction term with  $i = 1$ . These three contributions yield the three terms at the right-hand side of (1.4.5).

The hierarchy of equations (1.4.5) is the analogue of the *Born-Green-Yvon (BGY) hierarchy* for systems of neutral particles (sometimes this hierarchy is called *BBGKY*, with the additional letters standing for Bogolubov and Kirkwood). It is useful to regroup the terms in (1.4.5) as follows:

$$\begin{aligned} n^k \nabla_{\mathbf{r}_1} g^{(k)}(\mathbf{r}_1, \dots, \mathbf{r}_k) &= \\ &= -\beta n^k g^{(k)}(\mathbf{r}_1, \dots, \mathbf{r}_k) \nabla_{\mathbf{r}_1} \sum_{j=2}^k \frac{e^2}{4\pi |\mathbf{r}_1 - \mathbf{r}_j|} \\ &- \beta n^{k+1} \int_V d\mathbf{r}_{k+1} \left[ g^{(k+1)}(\mathbf{r}_1, \dots, \mathbf{r}_{k+1}) - g^{(k)}(\mathbf{r}_1, \dots, \mathbf{r}_k) \right] \times \\ &\quad \times \nabla_{\mathbf{r}_1} \frac{e^2}{4\pi |\mathbf{r}_1 - \mathbf{r}_{k+1}|} . \end{aligned} \quad (1.4.6)$$

The integral still depends on  $V$ , as in (1.4.5). However, in the thermodynamic limit the distribution function  $g^{(k+1)}(\mathbf{r}_1, \dots, \mathbf{r}_{k+1})$  is expected to reduce to  $g^{(k)}(\mathbf{r}_1, \dots, \mathbf{r}_k)$ , when  $\mathbf{r}_{k+1}$  is far from any of the positions  $\mathbf{r}_1, \dots, \mathbf{r}_k$ . The reason for this is that particles that are far apart will be uncorrelated. Although the Coulomb interaction is long-range, correlations between far particles are negligible for the OCP as they are for systems of neutral particles. If the convergence of  $g^{(k+1)}$  to  $g^{(k)}$  is sufficiently fast, the integrand in (1.4.6) vanishes for large  $\mathbf{r}_{k+1}$ , so that the integration may be extended to infinity. The precise conditions for the validity of (1.4.6) in the thermodynamic limit have been studied in [13].

The behaviour of the distribution functions for large interparticle distances comes to the fore if a *cluster decomposition* of  $g^{(k)}$  is made. For the first few values of  $k$  one writes:

$$g^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = 1 + h^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \quad , \quad (1.4.7)$$

$$\begin{aligned} g^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) &= \\ &= 1 + h^{(2)}(\mathbf{r}_1, \mathbf{r}_2) + h^{(2)}(\mathbf{r}_1, \mathbf{r}_3) + h^{(2)}(\mathbf{r}_2, \mathbf{r}_3) + h^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \quad , \end{aligned} \quad (1.4.8)$$

with the *Ursell functions*  $h^{(k)}$ . By definition one writes  $h^{(1)}(\mathbf{r}_1) = g^{(1)}(\mathbf{r}_1) = 1$ . For the general case one has:

$$g^{(k)} = \sum_{\{i_m\}} \prod_m h^{(i_m)} \quad , \quad (1.4.9)$$

with  $\sum_m i_m = k$ . The sum over the products of Ursell functions is found by dividing the  $k$  position vectors into groups in all different ways.

The behaviour of  $g^{(k)}$  for large values of any of its arguments is easily translated into a simple property of the Ursell functions, namely that the latter tend to 0 if any two position vectors are far apart. This is called the clustering property of the Ursell functions. As to the precise behaviour of the Ursell functions for large separations

“not much is rigorously known”, to cite a recent review [5]. For the OCP with small values of  $\Gamma$  one has proven (see [14] and [15]) that the Ursell functions are bounded by an exponential function of the form  $\exp(-CR)$ , if the position vectors  $\mathbf{r}_1, \dots, \mathbf{r}_k$  fall apart in two groups that are a (large) distance  $R$  apart. This is called *exponential clustering*. Usually one assumes that this exponential clustering remains true for the OCP with larger values of  $\Gamma$ . Incidentally, it may be remarked that it has been shown recently that exponential clustering is unlikely to be true for a quantum OCP [16].

For future reference we will write down explicitly the first two equations of the hierarchy (1.4.6). For  $k = 1$  we get:

$$\int d\mathbf{r}_2 h^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \nabla_{\mathbf{r}_1} \frac{e^2}{4\pi |\mathbf{r}_1 - \mathbf{r}_2|} = 0 \quad . \quad (1.4.10)$$

Using translation invariance we may write this identity as:

$$\int d\mathbf{r} h^{(2)}(|\mathbf{r}|) \nabla_{\mathbf{r}} \frac{e^2}{4\pi |\mathbf{r}|} = 0 \quad , \quad (1.4.11)$$

which is trivially true as a consequence of rotation invariance.

For  $k = 2$  the hierarchy equation gives:

$$\begin{aligned} \nabla_{\mathbf{r}_1} h^{(2)}(\mathbf{r}_1, \mathbf{r}_2) &= \\ &= -\beta \left[ 1 + h^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \right] \nabla_{\mathbf{r}_1} \frac{e^2}{4\pi |\mathbf{r}_1 - \mathbf{r}_2|} \\ &- \beta n \int d\mathbf{r}_3 \left[ h^{(2)}(\mathbf{r}_1, \mathbf{r}_3) + h^{(2)}(\mathbf{r}_2, \mathbf{r}_3) + h^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \right] \times \\ &\quad \times \nabla_{\mathbf{r}_1} \frac{e^2}{4\pi |\mathbf{r}_1 - \mathbf{r}_3|} \quad . \quad (1.4.12) \end{aligned}$$

The first term between the square brackets in the integrand can be skipped on account of (1.4.11). The resulting equation is a non-trivial identity relating two-particle and three-particle Ursell functions. In the following chapter we shall see how interesting information can be extracted from this equation. Before doing that we shall briefly consider an approximate theory that can be formulated for an OCP with small plasma parameter.

## 1.5 Debye-Hückel theory

Historically, the earliest attempts to give a statistical theory of Coulomb systems goes back to the work of Debye and Hückel on the properties of dilute electrolytes. They formulated a statistical theory for Coulomb system with small plasma parameter. In this section we shall review this theory for the OCP; in particular, we wish to show how in that approximate theory an explicit form for the two-particle Ursell function can be obtained.

The average charge density that is present at  $\mathbf{r}$ , if a charged particle resides in the origin, is given as:

$$en h^{(2)}(r) \quad . \quad (1.5.1)$$

The electrostatic potential  $\varphi(r)$  that is generated by this isotropic charge distribution satisfies the Poisson equation:

$$\Delta\varphi(r) = -en h^{(2)}(r) \quad . \quad (1.5.2)$$

For low densities it may be argued that this potential determines the pair distribution function through a simple Boltzmann factor:

$$\begin{aligned} g^{(2)}(r) &= e^{-\beta e\varphi(r)} = \\ &\simeq 1 - \beta e\varphi(r) \quad , \end{aligned} \quad (1.5.3)$$

where in the last step it has been assumed that the temperature is high and moreover that  $\varphi(r)$  is small. Combining (1.5.2) and (1.5.3) we find the Debye-Hückel equation:

$$\Delta\varphi(r) = \beta ne^2\varphi(r) \quad , \quad (1.5.4)$$

of which the solution is:

$$\varphi(r) = A \frac{e^{-k_D r}}{r} \quad , \quad (1.5.5)$$

with the Debye wave number  $k_D$  given by  $k_D^2 = \beta ne^2$ . Since for small values of  $r$  the potential should reduce to the Coulomb potential, the constant  $A$  must be equal to  $e/(4\pi)$ . Inserting (1.5.5) in (1.5.3) we arrive at the Debye-Hückel form for the Ursell function:

$$h_{DH}^{(2)}(r) = -\frac{\beta e^2}{4\pi r} e^{-k_D r} \quad . \quad (1.5.6)$$

The derivation shows that this form of the Ursell function can at most be approximately valid for low density and high temperature, i.e. for small plasma parameter. Moreover, it can not be true for small interparticle separations, since  $h^{(2)}$  then diverges according to (1.5.6), whereas it should go to  $-1$ . This deficiency of the Debye-Hückel result could be expected in view of the approximation made in (1.5.3). On the other hand, (1.5.6) can be expected to be a reliable approximation for the long-range behaviour of the Ursell function.

Introducing dimensionless variables the Debye-Hückel expression becomes:

$$h_{DH}^{(2)}(r) = -\frac{\Gamma}{\tilde{r}} e^{-\sqrt{3}\Gamma\tilde{r}} \quad , \quad (1.5.7)$$

with  $\tilde{r} \equiv |\tilde{\mathbf{r}}|$ . Indeed,  $h^{(2)}$  depends on  $\tilde{r}$  and  $\Gamma$  only, as has been stated below (1.4.4).

The Fourier transform of the Ursell function (1.5.6) is found to be

$$h_{DH}^{(2)}(k) = -\frac{\beta e^2}{k^2 + k_D^2} \quad , \quad (1.5.8)$$

which yields upon expansion for small wavenumber:

$$h_{DH}^{(2)}(k) = -\frac{1}{n} \left( 1 - \frac{k^2}{k_D^2} + \dots \right) \quad . \quad (1.5.9)$$

The Debye-Hückel Ursell function in Fourier space has a rather simple structure, which can not be expected to remain valid for an OCP with an arbitrary plasma

parameter. Nevertheless, we shall find in the next chapter that the first few terms of the expansion in powers of  $k$ , as given by (1.5.9), are completely general.

The Debye-Hückel approximation for  $h^{(2)}$  can be used to derive approximate expressions for the thermodynamic functions as well. In fact, since the dimensionless excess internal energy per particle  $\beta u^{exc}$  can be written as:

$$\beta u^{exc} = \frac{1}{2} n \beta \int d\mathbf{r} h^{(2)}(r) \frac{e^2}{4\pi r} \quad , \quad (1.5.10)$$

we have in dimensionless units:

$$\Gamma \frac{\partial \psi}{\partial \Gamma} = \frac{3\Gamma}{2} \int d\tilde{\mathbf{r}} \frac{1}{4\pi\tilde{r}} h^{(2)}(\tilde{r}) \quad . \quad (1.5.11)$$

Inserting (1.5.7) we obtain upon integration with respect to  $\Gamma$ :

$$\psi_{DH}(\Gamma) = - \left( \frac{\Gamma^3}{3} \right)^{1/2} \quad , \quad (1.5.12)$$

so that (1.3.6)–(1.3.7) become:

$$\beta u_{DH} = \frac{3}{2} - \frac{\sqrt{3}}{2} \Gamma^{3/2} \quad , \quad (1.5.13)$$

$$\frac{\beta p_{DH}}{n} = 1 - \frac{\sqrt{3}}{6} \Gamma^{3/2} \quad . \quad (1.5.14)$$

Let us conclude this section by remarking that the Debye-Hückel result is the first term in a systematic expansion of the Ursell function and the thermodynamic functions with respect to the plasma parameter. Higher-order terms have been derived by a resummation of the Mayer series. This resummation technique leads to the so-called “*nodal expansion*” [19] – [21]. One has found for instance [20] :

$$\beta u = \frac{3}{2} - \frac{\sqrt{3}}{2} \Gamma^{3/2} - \frac{9}{8} \Gamma^3 \log \Gamma - \Gamma^3 \left( \frac{3\gamma}{2} + \frac{9}{8} \log 3 - 1 \right) + \dots \quad , \quad (1.5.15)$$

with  $\gamma = 0.57722\dots$  the Euler constant. Clearly, the expansion in  $\Gamma$  is non-analytic. It should be remembered that  $\Gamma$  itself is non-analytic in  $n$ .



## Hoofdstuk 2

# Sum rules and fluctuation formulas

### 2.1 Perfect screening

The hierarchy equations can be used to derive so-called sum rules for the two-particle Ursell function (see [5], [17], [18]). These sum rules have the general form:

$$\int d\mathbf{r} r^{2n} h^{(2)}(r) = C_n \quad , \quad (2.1.1)$$

with positive integer  $n$  and constants  $C_n$ . In the following we shall see how  $C_n$  for low  $n$  can be evaluated quite generally for arbitrary  $\Gamma$ . In view of the scaling properties of  $h^{(2)}(r)$  the constants  $C_n$  must have the form  $\tilde{C}_n(\Gamma)a^{2n+3}$ .

Consider the integral in (1.4.12) with  $h^{(2)}(\mathbf{r}_2, \mathbf{r}_3)$  in the integrand. Introducing  $\mathbf{r} \equiv \mathbf{r}_1 - \mathbf{r}_2$  and  $\mathbf{r}' \equiv \mathbf{r}_3 - \mathbf{r}_2$  we may write it as:

$$- \int d\mathbf{r}' h^{(2)}(|\mathbf{r}'|) \nabla_{\mathbf{r}} \frac{e^2}{4\pi |\mathbf{r} - \mathbf{r}'|} \quad , \quad (2.1.2)$$

where we have suppressed a factor  $\beta n$ . This integral represents the electric field at the position  $\mathbf{r}$  generated by a charge distribution with density  $h^{(2)}(|\mathbf{r}'|)$ . Since the charge density is isotropic the electric field can conveniently be written as a superposition of the fields generated by spherical shells of radius  $|\mathbf{r}'|$ , each with a uniform charge distribution. As is well-known from electrostatics the shells with radius larger than  $|\mathbf{r}|$  can not contribute to the field, while the contributions of the shells with a radius smaller than  $|\mathbf{r}|$  can easily be determined by concentrating the total charge from each of these shells in the centre of the shell, i.e. in the origin. A formal proof of this theorem follows by using the Legendre polynomial expansion of the Coulomb potential:

$$\frac{1}{4\pi |\mathbf{r} - \mathbf{r}'|} = \sum_{\ell=0}^{\infty} \frac{|\mathbf{r}'|^\ell}{4\pi |\mathbf{r}|^{\ell+1}} P_\ell(\hat{\mathbf{r}} \cdot \hat{\mathbf{r}}') \quad , \quad (2.1.3)$$

for  $|\mathbf{r}'| < |\mathbf{r}|$ . (Here  $\hat{\mathbf{a}}$  denotes a unit vector in the direction of  $\mathbf{a}$ .) We may now write (2.1.2) as:

$$- \int_{|\mathbf{r}'| < |\mathbf{r}|} d\mathbf{r}' h^{(2)}(|\mathbf{r}'|) \nabla_{\mathbf{r}} \frac{e^2}{4\pi |\mathbf{r}|} \quad , \quad (2.1.4)$$

so that (1.4.12) becomes:

$$\begin{aligned} & \beta n \int d\mathbf{r}_3 h^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \nabla_{\mathbf{r}_1} \frac{e^2}{4\pi r_{13}} = \\ & = -\nabla_{\mathbf{r}_1} h^{(2)}(r_{12}) - \beta \left[ 1 + h^{(2)}(r_{12}) \right] \nabla_{\mathbf{r}_1} \frac{e^2}{4\pi r_{12}} \\ & \quad - \beta n \int_{r_{23} < r_{12}} d\mathbf{r}_3 h^{(2)}(r_{23}) \nabla_{\mathbf{r}_1} \frac{e^2}{4\pi r_{12}} \quad , \end{aligned} \quad (2.1.5)$$

with  $\mathbf{r}_{ij} \equiv \mathbf{r}_i - \mathbf{r}_j$  and  $r_{ij} \equiv |\mathbf{r}_{ij}|$ .

Let us now consider the behaviour of the various terms of (2.1.5) for large values of  $r_{12}$ . The left-hand side and both the first and third terms at the right-hand side then go to 0 exponentially fast. On the other hand, the second and the fourth term at the right-hand side decay rather slowly, so that these terms should compensate each other. Hence, we have found:

$$\int d\mathbf{r} h^{(2)}(r) = -\frac{1}{n} \quad . \quad (2.1.6)$$

This is the “*perfect-screening sum rule*”. (Sometimes it goes under the name of the “*electroneutrality sum rule*”.)

To interpret the sum rule we should remember that

$$ng^{(2)}(r) d\mathbf{r} \quad (2.1.7)$$

is the average number of particles in  $d\mathbf{r}$ , if a particle is present at the origin. Taking the background into account we conclude that the average charge in  $d\mathbf{r}$  is

$$neh^{(2)}(r) d\mathbf{r} \quad , \quad (2.1.8)$$

if a particle resides in the origin. The total average charge surrounding a particle in the origin with charge  $e$  is thus:

$$ne \int d\mathbf{r} h^{(2)}(r) \quad . \quad (2.1.9)$$

According to (2.1.6) the charge in the origin and in the surrounding cloud exactly cancel.

Incidentally, we remark that for systems of neutral particles a sum rule for  $h^{(2)}$  can be derived as well. It is the well-known *compressibility relation* (cf. (1.3.19)):

$$1 + n \int d\mathbf{r} h^{(2)}(r) = \frac{n\kappa T}{\beta} \quad . \quad (2.1.10)$$

Often the perfect-screening relation is written as a condition on the Fourier transform of  $h^{(2)}$ . Writing

$$h^{(2)}(r) = \int \frac{d\mathbf{k}}{(2\pi)^3} e^{i\mathbf{k}\cdot\mathbf{r}} h^{(2)}(k) \quad , \quad (2.1.11)$$

one finds:

$$h^{(2)}(0) = -\frac{1}{n} . \quad (2.1.12)$$

This result for the leading term in the expansion of the two-particle Ursell function in powers of  $k$  confirms the result found in the Debye-Hückel theory (see (1.5.9)). Perfect screening is correctly predicted by the Debye-Hückel theory.

A slightly different way to interpret the perfect-screening sum rule follows by relating it to density fluctuations. In fact, by introducing the local density fluctuation at position  $\mathbf{r}$  through:

$$\delta n(\mathbf{r}) = \sum_i \delta(\mathbf{r} - \mathbf{r}_i) - n , \quad (2.1.13)$$

one finds in the usual way for the scattering function:

$$nS(|\mathbf{r} - \mathbf{r}'|) \equiv \langle \delta n(\mathbf{r}) \delta n(\mathbf{r}') \rangle = n\delta(\mathbf{r} - \mathbf{r}') + n^2 h^{(2)}(|\mathbf{r} - \mathbf{r}'|) . \quad (2.1.14)$$

In Fourier language the structure factor  $S(\mathbf{k})$  is:

$$S(\mathbf{k}) = S(k) = 1 + nh^{(2)}(k) . \quad (2.1.15)$$

The perfect-screening sum rule thus states that the structure factor is zero for vanishing wavenumber. In other words, large-scale density fluctuations do not occur.

Finally, we return to (2.1.5). By employing (2.1.6) we may rewrite it as:

$$\begin{aligned} \beta n \int d\mathbf{r}_3 h^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \nabla_{\mathbf{r}_1} \frac{e^2}{4\pi r_{13}} &= -\nabla_{\mathbf{r}_1} h^{(2)}(r_{12}) \\ &- \beta \left[ h^{(2)}(r_{12}) - n \int_{r_{23} > r_{12}} d\mathbf{r}_3 h^{(2)}(r_{23}) \right] \nabla_{\mathbf{r}_1} \frac{e^2}{4\pi r_{12}} . \end{aligned} \quad (2.1.16)$$

Let us take the inner product of both sides with  $\mathbf{r}_{12}$  and integrate over  $\mathbf{r}_{12}$ . We then find:

$$\begin{aligned} -\beta n \int d\mathbf{r}_{12} d\mathbf{r}_{13} h^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \frac{e^2 \mathbf{r}_{12} \cdot \mathbf{r}_{13}}{4\pi r_{13}^3} &= - \int d\mathbf{r}_{12} \mathbf{r}_{12} \cdot \nabla_{\mathbf{r}_1} h^{(2)}(r_{12}) \\ &+ \beta \int d\mathbf{r}_{12} \left[ h^{(2)}(r_{12}) - n \int_{r_{23} > r_{12}} d\mathbf{r}_3 h^{(2)}(r_{23}) \right] \frac{e^2}{4\pi r_{12}} . \end{aligned} \quad (2.1.17)$$

The first term at the right-hand side is readily evaluated by integrating partially and employing perfect screening. In the last term at the right-hand side we may interchange the order of integration and perform the integral over  $\mathbf{r}_{12}$ . In this way we arrive at the identity:

$$\begin{aligned} -\beta n \int d\mathbf{r}_{12} d\mathbf{r}_{13} h^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \frac{e^2 \mathbf{r}_{12} \cdot \mathbf{r}_{13}}{4\pi r_{13}^3} &= -\frac{3}{n} \\ &+ \beta \int d\mathbf{r}_{12} h^{(2)}(r_{12}) \frac{e^2}{4\pi r_{12}} - \frac{1}{2} \beta n e^2 \int d\mathbf{r}_{12} r_{12}^2 h^{(2)}(r_{12}) , \end{aligned} \quad (2.1.18)$$

a result which we shall need in the next section.

## 2.2 Higher-order sum rules

We have seen above that in the Debye-Hückel approximation the Fourier representation of the two-particle Ursell function can be expanded for small wavenumber in even powers of  $k$ . The  $k^0$  term in this expansion agrees with the perfect-screening rule, while the coefficient of the second-order term is determined by the Debye wavenumber. Remarkably enough, one may derive this second-order coefficient quite generally by a systematic exploitation of the hierarchy equations up to third order [17], [18].

We start from the hierarchy equation (1.4.6) for  $k = 3$  with the cluster decomposition (1.4.9) inserted. If (1.4.12) is employed to eliminate the derivatives of the two-point cluster functions and use is made of (1.4.11) as well, we arrive at an expression for the derivative of the three-point cluster function:

$$\begin{aligned}
\nabla_{\mathbf{r}_1} h^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) &= \\
&= -\beta \left[ h^{(2)}(\mathbf{r}_2, \mathbf{r}_3) + h^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \right] \nabla_{\mathbf{r}_1} \left[ \frac{e^2}{4\pi |\mathbf{r}_1 - \mathbf{r}_2|} + \frac{e^2}{4\pi |\mathbf{r}_1 - \mathbf{r}_3|} \right] \\
&- \beta h^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \nabla_{\mathbf{r}_1} \left[ \frac{e^2}{4\pi |\mathbf{r}_1 - \mathbf{r}_3|} + n \int d\mathbf{r}_4 h^{(2)}(\mathbf{r}_3, \mathbf{r}_4) \frac{e^2}{4\pi |\mathbf{r}_1 - \mathbf{r}_4|} \right] \\
&- \beta h^{(2)}(\mathbf{r}_1, \mathbf{r}_3) \nabla_{\mathbf{r}_1} \left[ \frac{e^2}{4\pi |\mathbf{r}_1 - \mathbf{r}_2|} + n \int d\mathbf{r}_4 h^{(2)}(\mathbf{r}_2, \mathbf{r}_4) \frac{e^2}{4\pi |\mathbf{r}_1 - \mathbf{r}_4|} \right] \\
&- \beta n \int d\mathbf{r}_4 \left[ h^{(3)}(\mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4) + h^{(4)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4) \right] \nabla_{\mathbf{r}_1} \frac{e^2}{4\pi |\mathbf{r}_1 - \mathbf{r}_4|} \quad . \quad (2.2.1)
\end{aligned}$$

As in the previous section we now focus on the behaviour of the terms in this identity for large  $\mathbf{r}_1$ , or more precisely, for large  $\mathbf{r}_{12}$  and  $\mathbf{r}_{13}$ , while  $\mathbf{r}_{23}$  is kept constant. In that limit only a few terms decay slowly, namely the terms with  $h^{(2)}$  in the first line at the right-hand side and the contribution of  $h^{(3)}$  in the last integral. Since these terms must compensate we find for large  $\mathbf{r}_{12}$  and  $\mathbf{r}_{13}$ :

$$n \int d\mathbf{r}_4 h^{(3)}(\mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4) \frac{e^2}{4\pi r_{14}} = -h^{(2)}(r_{23}) \left[ \frac{e^2}{4\pi r_{12}} + \frac{e^2}{4\pi r_{13}} \right] \quad , \quad (2.2.2)$$

where we omitted a  $\nabla$ -operator common to both sides of the equation (the behaviour for infinite  $\mathbf{r}_1$  fixes an additive constant to be 0).

The Coulomb potentials depending on  $r_{13}$  and on  $r_{14}$  can be expanded with the help of the Legendre formula (2.1.3). Comparison of the terms of leading order in  $r_{12}$  yields:

$$n \int d\mathbf{r}_3 h^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = -2h^{(2)}(r_{12}) \quad , \quad (2.2.3)$$

where we changed the labels of the position vectors ( $2 \rightarrow 1, 3 \rightarrow 2, 4 \rightarrow 3$ ). This relation is the generalization of the perfect-screening sum rule to the three-particle Ursell function.

Further relations follow from the higher-order terms in the Legendre expansions for (2.2.2). From the  $\ell = 1, 2$  terms we get:

$$n \int d\mathbf{r}_3 h^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \mathbf{r}_{13} = -h^{(2)}(r_{12}) \mathbf{r}_{12} \quad , \quad (2.2.4)$$

$$n \int d\mathbf{r}_3 h^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \left[ 3(\mathbf{r}_{12} \cdot \mathbf{r}_{13})^2 - r_{12}^2 r_{13}^2 \right] = -2h^{(2)}(r_{12}) r_{12}^4 \quad . \quad (2.2.5)$$

The first of these identities will be used presently to derive a new sum rule for  $h^{(2)}$ , while the second will be employed in the derivation of fluctuation formulas in section 2.4.

In view of (2.1.18) we take the inner product of (2.2.4) with  $\mathbf{r}_{12}/(4\pi r_{12}^3)$  and integrate over  $\mathbf{r}_{12}$ , with the result:

$$n \int d\mathbf{r}_{12} d\mathbf{r}_{13} h^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \frac{\mathbf{r}_{12} \cdot \mathbf{r}_{13}}{4\pi r_{13}^3} = - \int d\mathbf{r}_{12} h^{(2)}(r_{12}) \frac{1}{4\pi r_{12}} \quad , \quad (2.2.6)$$

where we interchanged the indices 2 and 3 in the integral at the left-hand side, so as to get complete agreement with the left-hand side of (2.1.18). Combining the two equations we end up with a simple relation for  $h^{(2)}$ :

$$\int d\mathbf{r} r^2 h^{(2)}(r) = -\frac{6}{nk_D^2} \quad . \quad (2.2.7)$$

where we introduced the Debye wavenumber  $k_D = (\beta n e^2)^{1/2}$ . This is the second-order sum rule of Stillinger and Lovett [22]. Taking the Fourier transform we get:

$$\left. \frac{d^2}{dk^2} h^{(2)}(k) \right|_{k=0} = \frac{2}{nk_D^2} \quad , \quad (2.2.8)$$

so that the expansion of  $h(k)$  up to second order in  $k$  becomes:

$$h^{(2)}(k) = -\frac{1}{n} \left( 1 - \frac{k^2}{k_D^2} + \dots \right) \quad . \quad (2.2.9)$$

The result (1.5.9), which has been derived from the Debye-Hückel theory, is thus valid for arbitrarily dense one-component plasmas. In terms of the structure factor (2.1.15) we have found:

$$S(k) = \frac{k^2}{k_D^2} + \dots \quad . \quad (2.2.10)$$

Although large-scale density fluctuations are suppressed in the OCP, fluctuations on the scale of the Debye length  $k_D^{-1}$  may occur.

The second-order sum rule that has been derived here does not yet exhaust the amount of information that can be extracted from the hierarchy equations. In fact, even the fourth-order term in the expansion of  $h^{(2)}(k)$  or  $S(k)$  with respect to  $k$  can be determined in this way. We give the final result without proof:

$$S(k) = \frac{k^2}{k_D^2} - \frac{\beta}{n\kappa_T} \frac{k^4}{k_D^4} + \dots \quad . \quad (2.2.11)$$

Hence, the (dimensionless) isothermal compressibility finally appears in (the denominator of) the fourth-order term, whereas for a system of neutral particles it shows up already in the zeroth-order term (see (2.1.10)).

### 2.3 The direct correlation function

An alternative way to describe the properties of the two-particle equilibrium correlations in the OCP makes use of the *direct correlation function*  $c(r)$ . It is defined in terms of the two-particle cluster function  $h^{(2)}$  through the *Ornstein-Zernike equation*:

$$\int d\mathbf{r}' \left[ \delta(\mathbf{r} - \mathbf{r}') + nh^{(2)}(|\mathbf{r} - \mathbf{r}'|) \right] \left[ \delta(\mathbf{r}' - \mathbf{r}'') - nc(|\mathbf{r}' - \mathbf{r}''|) \right] = \delta(\mathbf{r} - \mathbf{r}'') \quad , \quad (2.3.1)$$

or in Fourier language:

$$1 - nc(k) = \frac{1}{1 + nh^{(2)}(k)} = \frac{1}{S(k)} \quad . \quad (2.3.2)$$

Inserting (2.2.11) we get the expansion:

$$c(k) = -\frac{1}{n} \left[ \frac{k_D^2}{k^2} - 1 + \frac{\beta}{n\kappa_T} + \dots \right] \quad . \quad (2.3.3)$$

For small  $k$  the direct correlation function is thus divergent. It is proportional to the Fourier transform of the Coulomb potential:

$$c(k) = -\frac{\beta e^2}{k^2} + \dots = -\beta\varphi(k) + \dots \quad . \quad (2.3.4)$$

For fluids of neutral particles it can be made plausible by means of diagram expansions that for large  $r$  one should have  $c(r) \simeq -\beta\varphi(r)$  (see [23]). Here we have derived a similar relation for the OCP. In the past the behaviour of the structure factor has sometimes [24] been obtained by postulating the general validity of (2.3.4) as a starting-point. In the present context it has emerged as a corollary of a set of results that were derived from first principles like the hierarchy equations.

The direct correlation function can be employed as a starting-point for the formulation of approximation schemes that aim at an evaluation of the static properties of the OCP for arbitrary plasma parameter. A well-known scheme that yields rather nice results is the *hypernetted-chain equation (HNC)* [25]. On the basis of a diagram expansion one may write:

$$c(r) = -\beta\varphi(r) + h^{(2)}(r) - \log g^{(2)}(r) + B(r) \quad , \quad (2.3.5)$$

where  $B(r)$  is the contribution of the so-called *bridge* diagrams. For large  $r$  this contribution can be neglected. Since moreover both  $h^{(2)}(r)$  and  $g^{(2)}(r)$  vanish for large  $r$  the approximate relation  $c(r) \simeq -\beta\varphi(r)$  is indeed recovered. The bridge diagrams are difficult to evaluate. In the HNC scheme they are simply omitted, for all  $r$ , so that one is left with the basic HNC relation:

$$c(r) = -\beta\varphi(r) + h^{(2)}(r) - \log g^{(2)}(r) \quad . \quad (2.3.6)$$

In combination with the Ornstein-Zernike equation this relation is sufficient to determine both  $c(r)$  and  $h^{(2)}(r)$  through numerical solution of an integral equation. The results are in remarkably good agreement with the data obtained through computer simulations (Monte Carlo). Further refinements with the use of density functional theories [26] have led to an almost perfect agreement, as can be seen from the example given in Figure 2.1.

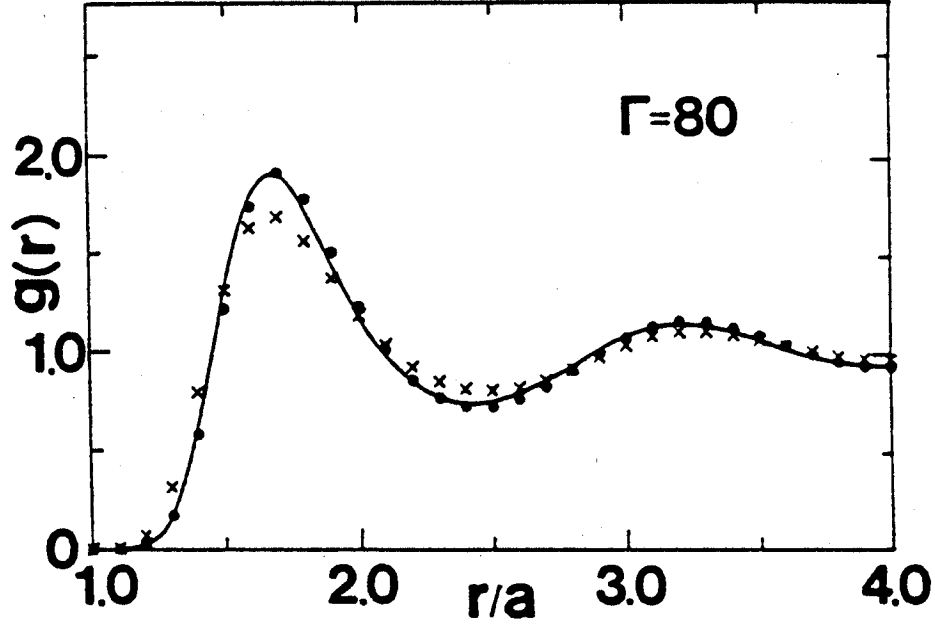


Figure 2.1: Radial distribution functions  $g^{(2)}(r)$  at  $\Gamma = 80$ . Filled circles represent MC values, crosses the HNC data. The solid curve depicts the improved HNC results obtained by using density-functional methods.

## 2.4 Fluctuation formulas involving particle, momentum and energy density

In studying the collective modes of the OCP we shall need information on large-scale fluctuations of the conserved quantities of the system, i.e. the particle density, the momentum density and the energy density. The complete set of formulas for these fluctuations will be collected in this section.

We start with a simple case: *density* fluctuations. Large-scale density fluctuations are suppressed in an OCP, as we have seen in section 2.1. Generally, density fluctuations are connected to the scattering function  $S(|\mathbf{r} - \mathbf{r}'|)$  according to (2.1.14). A convenient way to write that connexion follows by introducing the Fourier transform of the local density fluctuation (2.1.13):

$$\delta n(\mathbf{k}) = \sum_i e^{-i\mathbf{k}\cdot\mathbf{r}_i} \quad (2.4.1)$$

for  $\mathbf{k} \neq \mathbf{0}$ . In terms of these Fourier-transformed fluctuations the relation (2.1.14) reads:

$$nS(k) = \int d(\mathbf{r} - \mathbf{r}') e^{-i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')} \langle \delta n(\mathbf{r})\delta n(\mathbf{r}') \rangle =$$

$$\begin{aligned}
&= \frac{1}{V} \int_V d\mathbf{r} \int_V d\mathbf{r}' e^{-i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')} \langle \delta n(\mathbf{r}) \delta n(\mathbf{r}') \rangle = \\
&= \frac{1}{V} \langle [\delta n(\mathbf{k})]^* \delta n(\mathbf{k}) \rangle \quad . \quad (2.4.2)
\end{aligned}$$

Using (2.2.10) we get:

$$\frac{1}{V} \langle [\delta n(\mathbf{k})]^* \delta n(\mathbf{k}) \rangle = n \frac{k^2}{k_D^2} + \dots \quad , \quad (2.4.3)$$

for small  $\mathbf{k}$ .

Fluctuations  $\delta \mathbf{g}(\mathbf{r}) \equiv \mathbf{g}(\mathbf{r}) - \langle \mathbf{g}(\mathbf{r}) \rangle = \mathbf{g}(\mathbf{r})$  in the local *momentum* density

$$\mathbf{g}(\mathbf{r}) = \sum_i \mathbf{p}_i \delta(\mathbf{r} - \mathbf{r}_i) \quad , \quad (2.4.4)$$

are given in Fourier space as:

$$\delta \mathbf{g}(\mathbf{k}) = \sum_i \mathbf{p}_i e^{-i\mathbf{k}\cdot\mathbf{r}_i} \quad . \quad (2.4.5)$$

They are readily found to be governed by the formula (valid for all  $\mathbf{k}$ ):

$$\frac{1}{V} \langle [\delta \mathbf{g}(\mathbf{k})]^* \delta \mathbf{g}(\mathbf{k}) \rangle = \frac{nm}{\beta} \mathbf{U} \quad , \quad (2.4.6)$$

with  $\mathbf{U}$  the unit tensor.

To study *energy* density fluctuations we first have to define a local energy density  $\varepsilon(\mathbf{r})$  for the OCP. Of course, the energy density is the sum of a kinetic and a potential contribution:

$$\varepsilon(\mathbf{r}) = \varepsilon^{kin}(\mathbf{r}) + \varepsilon^{pot}(\mathbf{r}) \quad . \quad (2.4.7)$$

The kinetic energy density is trivially defined as:

$$\varepsilon^{kin}(\mathbf{r}) = \sum_i \frac{p_i^2}{2m} \delta(\mathbf{r} - \mathbf{r}_i) \quad . \quad (2.4.8)$$

In contrast, the potential (Coulomb) energy of the system can be localized in various ways. A convenient way to define  $\varepsilon^{pot}(\mathbf{r})$  follows by localizing the Coulomb energy of a pair of particles half at one particle and half at the other:

$$\begin{aligned}
\varepsilon^{pot}(\mathbf{r}) &= \frac{1}{2} \int_V d\mathbf{r}' \frac{e^2}{4\pi |\mathbf{r} - \mathbf{r}'|} \times \\
&\times \left[ \sum'_{i,j} \delta(\mathbf{r} - \mathbf{r}_i) \delta(\mathbf{r}' - \mathbf{r}_j) - n \sum_i \delta(\mathbf{r} - \mathbf{r}_i) - n \sum_j \delta(\mathbf{r}' - \mathbf{r}_j) + n^2 \right] \quad . \quad (2.4.9)
\end{aligned}$$

Clearly, integration over the volume  $\int_V d\mathbf{r} \varepsilon(\mathbf{r})$  yields the Hamiltonian  $H_N$  defined in (1.2.1), as it should be.

An alternative way to define a local potential energy density starts from the well-known energy density  $(1/2)E^2$ , with  $E$  the electric field generated by the charges of



the system. Since the electric field extends to regions of space outside the volume  $V$  the total potential energy  $\Phi_N$  is not obtained completely by merely integrating  $(1/2)E^2$  over  $V$ . Nevertheless, one can show [17] that owing to the presence of the neutralizing background the large-scale fluctuations of the energy density (2.4.9) are governed by the same formulas as are the fluctuations of  $(1/2)E^2$ , apart from terms that are of higher order in the wavenumber.

The Fourier transform of the energy density fluctuation  $\delta\varepsilon(\mathbf{r}) \equiv \varepsilon(\mathbf{r}) - \langle \varepsilon(\mathbf{r}) \rangle = \varepsilon(\mathbf{r}) - nu$  satisfies a fluctuation formula for small wavenumber that is obtained in the well-known fashion by differentiating the expression for the average total energy:

$$\frac{1}{V} \langle [\delta\varepsilon(\mathbf{k})]^* \delta\varepsilon(\mathbf{k}) \rangle = \frac{nc_v}{k_B \beta^2} \quad , \quad (2.4.10)$$

for small  $\mathbf{k}$ .

Finally, we consider the *cross-fluctuation formulas* involving products of two different fluctuations chosen from  $\delta n(\mathbf{k})$ ,  $\delta \mathbf{g}(\mathbf{k})$  and  $\delta\varepsilon(\mathbf{k})$ . Obviously, two of these cross-fluctuation formulas are trivial:

$$\frac{1}{V} \langle [\delta n(\mathbf{k})]^* \delta \mathbf{g}(\mathbf{k}) \rangle = 0 \quad , \quad (2.4.11)$$

$$\frac{1}{V} \langle [\delta\varepsilon(\mathbf{k})]^* \delta \mathbf{g}(\mathbf{k}) \rangle = 0 \quad , \quad (2.4.12)$$

since averages containing an uneven number of momenta vanish identically.

In contrast, the cross-fluctuation formula for the product of particle density and energy density fluctuations is non-trivial [17], [18], [27]. Starting in position space we first write the fluctuation expression as the sum of a kinetic and a potential contribution:

$$\langle \delta n(\mathbf{r}) \delta\varepsilon(\mathbf{r}') \rangle = \langle \delta n(\mathbf{r}) \delta\varepsilon^{kin}(\mathbf{r}') \rangle + \langle \delta n(\mathbf{r}) \delta\varepsilon^{pot}(\mathbf{r}') \rangle \quad . \quad (2.4.13)$$

The kinetic contribution is trivially related to the density fluctuation formula:

$$\langle \delta n(\mathbf{r}) \delta\varepsilon^{kin}(\mathbf{r}') \rangle = \frac{3}{2\beta} \langle \delta n(\mathbf{r}) \delta n(\mathbf{r}') \rangle \quad . \quad (2.4.14)$$

In Fourier space one thus finds:

$$\frac{1}{V} \langle [\delta n(\mathbf{k})]^* \delta\varepsilon^{kin}(\mathbf{k}) \rangle = \frac{3n}{2\beta} \frac{k^2}{k_D^2} + \dots \quad (2.4.15)$$

The potential contribution in (2.4.13) is given by an expression involving two- and three-particle Ursell functions:

$$\begin{aligned} \langle \delta n(\mathbf{r}) \delta\varepsilon^{pot}(\mathbf{r}') \rangle &= \frac{1}{2} n^3 \int d\mathbf{r}'' \frac{e^2}{4\pi |\mathbf{r}' - \mathbf{r}''|} h^{(3)}(\mathbf{r}, \mathbf{r}', \mathbf{r}'') \\ &+ \frac{1}{2} n^2 \delta(\mathbf{r} - \mathbf{r}') \int d\mathbf{r}'' \frac{e^2}{4\pi |\mathbf{r} - \mathbf{r}''|} h^{(2)}(\mathbf{r}, \mathbf{r}'') \\ &+ \frac{1}{2} n^2 \frac{e^2}{4\pi |\mathbf{r} - \mathbf{r}'|} h^{(2)}(\mathbf{r}, \mathbf{r}') \quad . \end{aligned} \quad (2.4.16)$$

Employing the symmetry of the three-particle Ursell function in its arguments and the identities (2.1.18) and (2.2.7) one can establish the relation [17], [18]:

$$\int d\mathbf{r}_{12} d\mathbf{r}_3 h^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \frac{e^2}{4\pi r_{12}} = -\frac{2}{n} \int d\mathbf{r}_{12} h^{(2)}(r_{12}) \frac{e^2}{4\pi r_{12}} \quad . \quad (2.4.17)$$

Integrating (2.4.16) over  $\mathbf{r} - \mathbf{r}'$  and using (2.4.17) we find in Fourier space:

$$\frac{1}{V} \langle [\delta n(\mathbf{k})]^* \delta \varepsilon^{pot}(\mathbf{k}) \rangle = 0 \quad , \quad (2.4.18)$$

in leading order of  $\mathbf{k}$ . We can even get a higher-order result by invoking the fourth-order sum rule (2.2.11) and employing similar tricks as above (in particular the relation (2.2.5))[17], [18]. The result is:

$$\frac{1}{V} \langle [\delta n(\mathbf{k})]^* \delta \varepsilon^{pot}(\mathbf{k}) \rangle = -\frac{3n}{\beta} \left( 1 - \frac{\beta}{n \kappa_T} \right) \frac{k^2}{k_D^2} + \dots \quad , \quad (2.4.19)$$

for small  $\mathbf{k}$ . Adding (2.4.15) and (2.4.19) we finally arrive at the cross-fluctuation formula:

$$\frac{1}{V} \langle [\delta n(\mathbf{k})]^* \delta \varepsilon(\mathbf{k}) \rangle = -\frac{3n}{2\beta} \left( 1 - \frac{2\beta}{n \kappa_T} \right) \frac{k^2}{k_D^2} + \dots \quad , \quad (2.4.20)$$

for small  $\mathbf{k}$ . Incidentally, we remark that the right-hand side can be written in a suggestive way by using the thermodynamic relation:

$$\left( \frac{\partial(nu)}{\partial n} \right)_\beta = \frac{3}{n \kappa_T} - \frac{3}{2\beta} \quad , \quad (2.4.21)$$

which follows from the equation of state (1.3.10). With this identity we get instead of (2.4.20):

$$\frac{1}{V} \langle [\delta n(\mathbf{k})]^* \delta \varepsilon(\mathbf{k}) \rangle = n \left( \frac{\partial(nu)}{\partial n} \right)_\beta \frac{k^2}{k_D^2} + \dots \quad , \quad (2.4.22)$$

which should be compared to (2.4.3).

Of course, the fact that the cross-fluctuation formula (2.4.20) or (2.4.22) starts with a term of order  $k^2$  is not an accident, since large-scale fluctuations in the particle density are anyhow suppressed in the OCP. Indeed, one may prove quite generally that all other cross-fluctuation formulas with the particle density (e.g. the density-pressure cross-fluctuation formula) start with a term of order  $k^2$ .

The complete set of small  $\mathbf{k}$  fluctuation formulas for the particle, momentum and energy density are now at our disposal. They are essential in studying the non-equilibrium properties of the OCP, to which we will now turn our attention.

## Hoofdstuk 3

# Collective modes

### 3.1 Balance equations

The non-equilibrium behaviour of a system, in particular the decay of time-dependent correlations, is largely governed by the collective modes that can be sustained in the system. In turn, these modes are determined by the conserved quantities. For a fluid of neutral particles there are five such conserved quantities: the particle number, the three components of the total momentum and the total energy. The corresponding local quantities for the OCP, viz. the particle density  $n(\mathbf{r})$ , the momentum density  $\mathbf{g}(\mathbf{r})$  and the energy density  $\varepsilon(\mathbf{r})$ , have already been defined in the previous sections. These local quantities satisfy balance equations which we shall study in this section.

The microscopic particle density

$$n(\mathbf{r}) = \sum_i \delta(\mathbf{r} - \mathbf{r}_i) \quad (3.1.1)$$

satisfies the continuity equation:

$$iL n(\mathbf{r}) = -\nabla_{\mathbf{r}} \cdot \frac{\mathbf{g}(\mathbf{r})}{m} \quad (3.1.2)$$

At the left-hand side we introduced the Liouville operator  $L$  which is defined such that the time derivative  $\dot{F}$  of an arbitrary phase function  $F(\mathbf{r}^N, \mathbf{p}^N)$  is given by  $iL F$ . The Liouville operator may be written in terms of a Poisson bracket with the Hamiltonian  $H_N$  of the system:  $iL \cdots = \{\cdots, H_N\}$ . At the right-hand side the momentum density as defined in (2.4.4) appears. Upon integration of (3.1.2) over  $\mathbf{r}$  it follows immediately that the total particle number is conserved, as it should be.

The Fourier transform of (3.1.2) is:

$$iL n(\mathbf{k}) = -i\mathbf{k} \cdot \frac{\mathbf{g}(\mathbf{k})}{m} \quad (3.1.3)$$

We shall use this balance equation for  $\mathbf{k} \neq \mathbf{0}$  only. Under that restriction the Fourier transformed particle density  $n(\mathbf{k})$  is given by the right-hand side of (2.4.1). Likewise, the Fourier transformed momentum density  $\mathbf{g}(\mathbf{k})$  is obtained from the right-hand side of (2.4.5).

The *momentum* balance equation in position space is obtained by differentiation of the microscopic momentum density (2.4.4). It reads:

$$iL \mathbf{g}(\mathbf{r}) = -\nabla_{\mathbf{r}} \cdot \boldsymbol{\tau}^{kin}(\mathbf{r}) + \sum_i \frac{\dot{\mathbf{p}}_i}{m} \delta(\mathbf{r} - \mathbf{r}_i) \quad , \quad (3.1.4)$$

with the microscopic kinetic pressure tensor:

$$\boldsymbol{\tau}^{kin}(\mathbf{r}) = \sum_i \frac{\mathbf{p}_i \mathbf{p}_i}{m} \delta(\mathbf{r} - \mathbf{r}_i) \quad . \quad (3.1.5)$$

To evaluate the last term of (3.1.4) we need the equation of motion of particle  $i$ :

$$\dot{\mathbf{p}}_i = e\mathbf{E}'(\mathbf{r}_i) \quad , \quad (3.1.6)$$

with  $\mathbf{E}'(\mathbf{r}_i)$  the electric field at the position  $\mathbf{r}_i$  that is generated by all particles except  $i$  and by the background. It is given as:

$$\mathbf{E}'(\mathbf{r}) = -\nabla_{\mathbf{r}} \left[ \sum_{j(\neq i)} \frac{e}{4\pi |\mathbf{r} - \mathbf{r}_j|} - \int_V d\mathbf{r}' \frac{ne}{4\pi |\mathbf{r} - \mathbf{r}'|} \right] \quad . \quad (3.1.7)$$

Inserting this expression in (3.1.6) and the result in (3.1.4) we can write the last term of the momentum balance equation as:

$$\begin{aligned} & - \int_V d\mathbf{r}' \left[ \nabla_{\mathbf{r}} \frac{e^2}{4\pi |\mathbf{r} - \mathbf{r}'|} \right] \left[ \sum'_{i,j} \delta(\mathbf{r} - \mathbf{r}_i) \delta(\mathbf{r}' - \mathbf{r}_j) \right. \\ & \left. - n \sum_i \delta(\mathbf{r} - \mathbf{r}_i) - n \sum_j \delta(\mathbf{r}' - \mathbf{r}_j) + n^2 \right] + \mathbf{f}(\mathbf{r}) \quad , \quad (3.1.8) \end{aligned}$$

Here we introduced the microscopic force density

$$\mathbf{f}(\mathbf{r}) = -n \int_V d\mathbf{r}' \left[ \nabla_{\mathbf{r}} \frac{e^2}{4\pi |\mathbf{r} - \mathbf{r}'|} \right] \left[ \sum_j \delta(\mathbf{r}' - \mathbf{r}_j) - n \right] \quad , \quad (3.1.9)$$

which describes (minus) the electric force on the background charge density  $-ne$  at  $\mathbf{r}$  due to density fluctuations at the position  $\mathbf{r}'$ . The remaining terms in (3.1.8) have the same structure as encountered in (2.4.9). These terms vanish upon integration over  $\mathbf{r}$ , as follows by employing the antisymmetry of the Coulomb force term in the integrand. On the other hand, the integral of the force density (3.1.9) over the volume  $V$  does not vanish identically: the background charge density can absorb momentum from the density fluctuations. This behaviour of the background is the reason for splitting off the force density  $\mathbf{f}(\mathbf{r})$  in (3.1.8). Clearly, upon integrating the balance equation (3.1.4) over  $\mathbf{r}$  one finds that the time derivative of the total momentum  $\int_V d\mathbf{r} \mathbf{g}(\mathbf{r})$  of the particles is given by minus the total force  $\int_V d\mathbf{r} \mathbf{f}(\mathbf{r})$  exerted on the background, which in general is not zero.

The special role played by the force density  $\mathbf{f}(\mathbf{r})$  becomes obvious by taking the Fourier transform of (3.1.4). One finds for  $\mathbf{k} \neq \mathbf{0}$ :

$$\begin{aligned} iL \mathbf{g}(\mathbf{k}) &= -ine^2 \frac{\mathbf{k}}{k^2} n(\mathbf{k}) - i\mathbf{k} \cdot \boldsymbol{\tau}^{kin}(\mathbf{k}) \\ &\quad - \int_V d\mathbf{r} e^{-i\mathbf{k} \cdot \mathbf{r}} \int_V d\mathbf{r}' \left[ \nabla_{\mathbf{r}} \frac{e^2}{4\pi |\mathbf{r} - \mathbf{r}'|} \right] \times \\ &\quad \times \left[ \sum'_{i,j} \delta(\mathbf{r} - \mathbf{r}_i) \delta(\mathbf{r}' - \mathbf{r}_j) - n \sum_i \delta(\mathbf{r} - \mathbf{r}_i) - n \sum_j \delta(\mathbf{r}' - \mathbf{r}_j) + n^2 \right]. \end{aligned} \quad (3.1.10)$$

The force density  $\mathbf{f}(\mathbf{r})$  has led to the first term at the right-hand side, which becomes arbitrary large for small  $\mathbf{k}$ . In contrast, the contribution of the kinetic pressure tensor goes to 0 for small  $\mathbf{k}$ . The same applies for the integral. In fact, it is proportional to  $-i\mathbf{k}$  for small  $\mathbf{k}$ , as can be seen by writing it as:

$$\begin{aligned} &-\frac{1}{2} \int_V d\mathbf{r} \int_V d\mathbf{r}' \left( e^{-i\mathbf{k} \cdot \mathbf{r}} - e^{-i\mathbf{k} \cdot \mathbf{r}'} \right) \left[ \nabla_{\mathbf{r}} \frac{e^2}{4\pi |\mathbf{r} - \mathbf{r}'|} \right] \times \\ &\times \left[ \sum'_{i,j} \delta(\mathbf{r} - \mathbf{r}_i) \delta(\mathbf{r}' - \mathbf{r}_j) - n \sum_i \delta(\mathbf{r} - \mathbf{r}_i) - n \sum_j \delta(\mathbf{r}' - \mathbf{r}_j) + n^2 \right]. \end{aligned} \quad (3.1.11)$$

Using a well-known trick we rewrite the difference of the two exponentials as:

$$-i\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}') e^{-\frac{1}{2}i\mathbf{k} \cdot (\mathbf{r} + \mathbf{r}')} \int_{-1/2}^{1/2} d\lambda e^{-i\lambda\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}')} \quad , \quad (3.1.12)$$

which shows that (3.1.11) is indeed proportional to  $-i\mathbf{k}$ . Writing it as  $-i\mathbf{k} \cdot \boldsymbol{\tau}^{pot}(\mathbf{k})$  the momentum balance equation in Fourier space gets the final form:

$$iL \mathbf{g}(\mathbf{k}) = -ine^2 \frac{\mathbf{k}}{k^2} n(\mathbf{k}) - i\mathbf{k} \cdot \boldsymbol{\tau}(\mathbf{k}) \quad , \quad (3.1.13)$$

with the total microscopic pressure tensor

$$\boldsymbol{\tau}(\mathbf{k}) \equiv \boldsymbol{\tau}^{kin}(\mathbf{k}) + \boldsymbol{\tau}^{pot}(\mathbf{k}) \quad . \quad (3.1.14)$$

Finally, we turn to the *energy* balance equation. Using similar techniques as above one can prove that the time derivative of the microscopic energy density (2.4.7) is given by (minus) the divergence of an energy current density  $\mathbf{j}_\varepsilon(\mathbf{r})$ . In Fourier space the energy balance equation reads:

$$iL \varepsilon(\mathbf{k}) = -i\mathbf{k} \cdot \mathbf{j}_\varepsilon(\mathbf{k}) \quad , \quad (3.1.15)$$

for  $\mathbf{k} \neq \mathbf{0}$ . An explicit expression for the energy current density will not be needed in the following.

### 3.2 Projection-operator formalism

As we have stated already in the beginning of the previous section an important tool in studying the non-equilibrium properties of a system like the OCP is the set of collective modes. To derive these modes we shall employ a projection operator technique [28], [29].

The time evolution of an arbitrary phase function  $F$  that may depend on  $\mathbf{r}$  follows by applying the Liouville operator:

$$F(\mathbf{r}, t) = e^{iLt} F(\mathbf{r}) \quad . \quad (3.2.1)$$

In Fourier language we have:

$$F(\mathbf{k}, t) = e^{iLt} F(\mathbf{k}) \quad . \quad (3.2.2)$$

We will be interested in particular in the time evolution of  $F$  for small  $\mathbf{k}$ . Upon introducing a one-sided Fourier transform with respect to  $t$  by writing:

$$F(\mathbf{k}, z) = -i \int_0^\infty dt e^{izt} F(\mathbf{k}, t) \quad , \quad (3.2.3)$$

for  $\text{Im } z > 0$ , we get:

$$(z + L) F(\mathbf{k}, z) = F(\mathbf{k}) \quad . \quad (3.2.4)$$

If  $F(\mathbf{k})$  is a linear combination of  $n(\mathbf{k})$ ,  $\mathbf{g}(\mathbf{k})$  and  $\varepsilon(\mathbf{k})$ , for which we derived the balance equations in the previous section, it will evolve rather slowly, since the Liouville operator is proportional to  $\mathbf{k}$  if acting on these quantities (the term in (3.1.13) that stems from the force density (3.1.9) seems to disturb this simple picture and will deserve careful discussion in the following).

To show explicitly the influence of the balance equations on the evolution of a function  $F(\mathbf{k})$  we will employ the projection operator formalism [30]. Let us choose five suitable linear independent combinations  $a_i(\mathbf{k})$  of the Fourier transformed particle density, momentum density and energy density (a specific choice will be made later on). Starting from these we define their adjoints  $\bar{a}_i(\mathbf{k})$  as linear combinations of the same quantities, with the orthogonality property:

$$\frac{1}{V} \langle [\bar{a}_i(\mathbf{k})]^* a_j(\mathbf{k}) \rangle = \delta_{ij} \quad . \quad (3.2.5)$$

For small  $\mathbf{k}$  the left-hand sides can be evaluated with the help of the fluctuation formulas, derived in section 2.4.

We now define a projection operator  $P$  by requiring that it projects a phase function  $F(\mathbf{k})$  on the space spanned by the basis  $a_i(\mathbf{k})$ :

$$P F(\mathbf{k}) = \sum_{i=1}^5 \frac{1}{V} \langle [\bar{a}_i(\mathbf{k})]^* F(\mathbf{k}) \rangle a_i(\mathbf{k}) \quad . \quad (3.2.6)$$

The complement  $1 - P$  of  $P$  will be denoted by  $Q$ . Clearly, if  $F$  is one of the basis functions  $a_i(\mathbf{k})$ , one has  $PF = F$ . As a consequence  $P$  is idempotent:  $P^2 = P$ , as expected for a projection operator.

Let us project both sides of (3.2.4) on the space complementary to that spanned by  $a_i(\mathbf{k})$ :

$$zQ F(\mathbf{k}, z) + QL(P + Q) F(\mathbf{k}, z) = Q F(\mathbf{k}) \quad , \quad (3.2.7)$$

or

$$Q F(\mathbf{k}, z) = -\frac{1}{z + QLQ} [QLP F(\mathbf{k}, z) - Q F(\mathbf{k})] \quad . \quad (3.2.8)$$

On the other hand, projection of (3.2.4) by means of  $P$  gives:

$$zP F(\mathbf{k}, z) + PL(P + Q) F(\mathbf{k}, z) = P F(\mathbf{k}) \quad , \quad (3.2.9)$$

which yields upon insertion of (3.2.8):

$$\left( z + PLP - PLQ \frac{1}{z + QLQ} QLP \right) P F(\mathbf{k}, z) = \left( P - PLQ \frac{1}{z + QLQ} Q \right) F(\mathbf{k}) \quad . \quad (3.2.10)$$

We now choose for  $F(\mathbf{k})$  one of the basis functions  $a_j(\mathbf{k})$ . Then we may write (3.2.10) as:

$$\sum_{i=1}^5 \left( z + PLP - PLQ \frac{1}{z + QLQ} QLP \right) a_i(\mathbf{k}) G_{ij}(\mathbf{k}, z) = a_j(\mathbf{k}) \quad , \quad (3.2.11)$$

with the propagator

$$G_{ij}(\mathbf{k}, z) = \frac{1}{V} \langle [\bar{a}_i(\mathbf{k})]^* a_j(\mathbf{k}, z) \rangle = \frac{1}{V} \left\langle [\bar{a}_i(\mathbf{k})]^* \frac{1}{z + L} a_j(\mathbf{k}) \right\rangle \quad . \quad (3.2.12)$$

Multiplying (3.2.11) by  $(1/V) [\bar{a}_\ell(\mathbf{k})]^*$  and taking the average we finally arrive at a matrix equation for the propagator:

$$\sum_{\ell} (z\delta_{i\ell} - \Omega_{i\ell}) G_{\ell j} = \delta_{ij} \quad , \quad (3.2.13)$$

with a frequency matrix  $\Omega_{ij}$  that is the sum of a “direct” and an “indirect” part:

$$\Omega_{ij}(\mathbf{k}, z) = \Omega_{ij}^{dir}(\mathbf{k}, z) + \Omega_{ij}^{ind}(\mathbf{k}, z) \quad . \quad (3.2.14)$$

These parts are defined as:

$$\Omega_{ij}^{dir}(\mathbf{k}, z) = -\frac{1}{V} \langle [\bar{a}_i(\mathbf{k})]^* L a_j(\mathbf{k}) \rangle \quad , \quad (3.2.15)$$

$$\Omega_{ij}^{ind}(\mathbf{k}, z) = \frac{1}{V} \left\langle [\bar{a}_i(\mathbf{k})]^* LQ \frac{1}{z + QLQ} QL a_j(\mathbf{k}) \right\rangle \quad . \quad (3.2.16)$$

The matrix equation (3.2.13) becomes trivially simple if the frequency matrix is diagonalized by adopting a suitable set of basis functions  $a_i(\mathbf{k})$ . As we shall see in the next section this diagonalization can be carried out explicitly by successive approximations for small  $\mathbf{k}$ . Once we have found a basis set for which  $\Omega_{ij}$  is diagonal (to a certain order in the wavenumber) we get from (3.2.13):

$$G_{ij}(\mathbf{k}, z) = \frac{\delta_{ij}}{z - z_i} \quad , \quad (3.2.17)$$

with  $z_i$  the eigenvalue of  $\Omega_{ij}$ . As a consequence (3.2.12) yields:

$$P a_i(\mathbf{k}, z) = \frac{1}{z - z_i} a_i(\mathbf{k}) \quad , \quad (3.2.18)$$

so that we get with the help of (3.2.8):

$$a_i(\mathbf{k}, z) = \left(1 - \frac{1}{z + QLQ} QL\right) \frac{1}{z - z_i} a_i(\mathbf{k}) \quad . \quad (3.2.19)$$

Hence, the time evolution of  $a_i(\mathbf{k})$  is completely known, at least in principle. This time evolution is governed by the position of the eigenvalue  $z_i$  in the complex plane and by the spectrum of the operator  $QLQ$ . We shall see that the eigenvalues  $z_i$  lie close to the real axis, at least for small  $\mathbf{k}$ . On the other hand, since  $Q$  projects onto the space that is orthogonal to the conserved quantities one expects that the spectrum of  $QLQ$  does not contain eigenvalues that are close to the real axis. Hence, the long-time behaviour of  $a_i(\mathbf{k}, t)$  is largely determined by the frequency  $z_i$ . The fundamental frequencies  $z_i$  are called the *mode frequencies* of the system. The corresponding functions  $a_i(\mathbf{k})$  are the *mode amplitudes*. In the next section both the amplitudes and the frequencies of the collective modes will be determined for small values of the wavenumber.

### 3.3 Collective modes

The amplitudes and frequencies of the collective modes are given by the eigenfunctions and eigenvalues of the frequency matrix (3.2.14). To determine these for the OCP we start by considering the eigenvalue problem in lowest order of the wavenumber, i.e. up to terms of order  $k^0$ . As a basis we choose the phase functions  $n(\mathbf{k})/k$ ,  $\mathbf{g}(\mathbf{k})$  and  $\varepsilon(\mathbf{k})$ . The extra factor  $k^{-1}$  in front of  $n(\mathbf{k})$  is added in view of the fluctuation formula (2.4.3). [It should be remembered that for any  $a$  the fluctuation  $\delta a(\mathbf{k})$  coincides with  $a(\mathbf{k})$  for  $\mathbf{k} \neq \mathbf{0}$ .] On account of the fluctuation formulas of section 2.4 the adjoints are found to be  $(k_D^2/n) n(\mathbf{k})/k$ ,  $[\beta/(nm)] \mathbf{g}(\mathbf{k})$  and  $[k_B \beta^2/(nc_v)] \varepsilon(\mathbf{k})$ , again in leading order of  $k$ .

Most elements of the matrix elements of the direct part of the frequency matrix vanish in order  $k^0$ , since the Liouville operator changes a phase function that is even in the momenta into one that is odd, and vice versa. The only matrix elements that are different from 0 are the off-diagonal elements connecting  $\mathbf{g}(\mathbf{k})$  with either  $n(\mathbf{k})/k$  or  $\varepsilon(\mathbf{k})$ . The first of these is trivially found:

$$-\frac{k_D^2}{nk} \frac{1}{V} \langle [n(\mathbf{k})]^* L \mathbf{g}(\mathbf{k}) \rangle = -\frac{k_D^2}{nk} \frac{1}{V} \langle [L n(\mathbf{k})]^* \mathbf{g}(\mathbf{k}) \rangle = \frac{k_D^2}{\beta} \hat{\mathbf{k}} \quad , \quad (3.3.1)$$

where we used the hermiticity of the Liouville operator, the continuity equation (3.1.3) and the fluctuation formula (2.4.6). The transposed matrix element differs only by a trivial factor:

$$-\frac{\beta}{nm} \frac{1}{V} \left\langle [\mathbf{g}(\mathbf{k})]^* L \frac{n(\mathbf{k})}{k} \right\rangle = \frac{1}{m} \hat{\mathbf{k}} \quad . \quad (3.3.2)$$



The second type of off-diagonal matrix elements that needs to be evaluated can be worked out with the use of the momentum balance equation (3.1.13):

$$-\frac{k_B\beta^2}{nc_v} \frac{1}{V} \langle [\varepsilon(\mathbf{k})]^* L \mathbf{g}(\mathbf{k}) \rangle = \frac{k_B\beta^2}{nc_v} \frac{1}{V} \left\langle [\varepsilon(\mathbf{k})]^* \left[ \mathbf{k} \cdot \boldsymbol{\tau}(\mathbf{k}) + ne^2 \frac{\mathbf{k}}{k^2} n(\mathbf{k}) \right] \right\rangle . \quad (3.3.3)$$

The right-hand side is the sum of two fluctuation expressions that are both of order  $k$ , so that they can be neglected for the moment. Of course, the transposed matrix element is of the same order.

Turning to the indirect part of the frequency matrix we immediately see that it is at least of order  $k^2$ . In fact,  $QL a_j(\mathbf{k})$  is of order  $k$  for all  $j$ , as follows by inspecting the balance equations. In particular, we must use that both  $Qn(\mathbf{k})$  and  $QLn(\mathbf{k})$  vanish identically.

In lowest order of  $k$  the frequency matrix has now been found as:

$$\Omega_{ij}(\mathbf{k}, z) = \begin{pmatrix} 0 & k_D^2 \hat{k}_x / \beta & k_D^2 \hat{k}_y / \beta & k_D^2 \hat{k}_z / \beta & 0 \\ \hat{k}_x / m & 0 & 0 & 0 & 0 \\ \hat{k}_y / m & 0 & 0 & 0 & 0 \\ \hat{k}_z / m & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{pmatrix} . \quad (3.3.4)$$

The eigenvalues of this frequency matrix follow from the characteristic equation:

$$z^3 \left( z^2 - \frac{k_D^2}{\beta m} \right) = 0 , \quad (3.3.5)$$

the solutions of which are:

$$z = 0 \quad (\text{threefold}) , \quad z = \pm \omega_p , \quad (3.3.6)$$

with the *plasma frequency*  $\omega_p = k_D / (\beta m)^{1/2} = (ne^2/m)^{1/2}$ . All five frequencies found here are real. Hence, the corresponding modes are not damped in the long-wavelength limit.

The mode amplitudes for the three degenerate modes with frequency  $z = 0$  are linear combinations of:

$$g_{\perp,i}(\mathbf{k}) \quad (i = 1, 2) , \quad \varepsilon(\mathbf{k}) . \quad (3.3.7)$$

Here  $g_{\perp,i}(\mathbf{k})$  denote the two (mutually orthogonal) components of the momentum density that are perpendicular to the wave vector. On account of rotation invariance one easily checks that the frequency matrix can not couple these transverse components of the momentum density to each other or to any of the other basis functions, for any value of  $\mathbf{k}$ . Hence, the correct zeroth-order mode amplitudes of the three modes that are degenerate in order  $k^0$  are indeed precisely those given in (3.3.7). Upon adding suitable normalization factors (such that the adjoint modes have the same form) we get:

$$a_{\perp,i}(\mathbf{k}) = \left( \frac{\beta}{nm} \right)^{1/2} g_{\perp,i}(\mathbf{k}) , \quad (3.3.8)$$

$$a_\varepsilon(\mathbf{k}) = \left( \frac{k_B \beta^2}{nc_v} \right)^{1/2} \varepsilon(\mathbf{k}) \quad . \quad (3.3.9)$$

Later on we shall see that we have found here the zeroth-order amplitudes of the *viscous* modes and the *heat* mode. Analogous modes occur in fluids of neutral particles.

The amplitudes of the modes with frequency  $\pm\omega_p$  in order  $k^0$  are proportional to:

$$\frac{1}{k} n(\mathbf{k}) \pm \frac{1}{m\omega_p} g_{\parallel}(\mathbf{k}) \quad , \quad (3.3.10)$$

with  $g_{\parallel}$  the component of the momentum density in the direction of the wave vector. Choosing a normalization factor such that the mode amplitude coincides with its adjoint we find:

$$a_{\pm}(\mathbf{k}) = \frac{1}{(2n)^{1/2}} \left[ \frac{k_D}{k} n(\mathbf{k}) \pm \left( \frac{\beta}{m} \right)^{1/2} g_{\parallel}(\mathbf{k}) \right] \quad . \quad (3.3.11)$$

These modes are called the *plasmon* modes or *plasmons*. Their occurrence is limited to charged-particle systems. In systems of neutral particles their place is taken by the sound modes the frequency of which is zero in the long-wavelength limit.

To understand the mechanism that leads to the plasmon modes we return to the balance equations of particle and momentum density. With the help of these we can write:

$$\begin{aligned} iLa_{\pm}(\mathbf{k}) &= \\ &= \frac{1}{(2n)^{1/2}} \left\{ -i \frac{k_D}{m} g_{\parallel}(\mathbf{k}) \pm \left( \frac{\beta}{m} \right)^{1/2} \left[ -i \frac{ne^2}{k} n(\mathbf{k}) - \frac{i}{k} \mathbf{k} \cdot \boldsymbol{\tau}(\mathbf{k}) \cdot \mathbf{k} \right] \right\} = \\ &= \mp i\omega_p a_{\pm}(\mathbf{k}) + \mathcal{O}(k) \quad . \end{aligned} \quad (3.3.12)$$

The interplay of the particle density and the longitudinal momentum density, and the particular role of the term with  $n(\mathbf{k})$  in the balance equation for  $g_{\parallel}(\mathbf{k})$  is clearly seen here.

Up to now we have limited ourselves to the leading-order terms in  $k$ . In concluding this section we shall briefly consider the *first-order* correction terms in the mode amplitudes and the mode frequencies. In first order of the wavenumber the adjoints of the basis functions  $n(\mathbf{k})/k$  and  $\varepsilon(\mathbf{k})$ , which were used in evaluating the frequency matrix, are no longer given by  $(k_D^2/n) n(\mathbf{k})/k$  and  $[k_B \beta^2 / (nc_v)] \varepsilon(\mathbf{k})$ , respectively; they acquire additional terms of order  $k$ . Furthermore, the contribution that has been written in (3.3.3) can no longer be neglected in order  $k$ . As a consequence the frequency matrix in first order of the wavenumber gets a few extra off-diagonal terms as compared to (3.3.4). It reads:

$$\Omega_{ij}(\mathbf{k}, z) = \begin{pmatrix} 0 & k_D^2 \hat{\mathbf{k}}/\beta & 0 \\ \hat{\mathbf{k}}/m & 0 & h\mathbf{k}/m \\ 0 & [1/3 + k_B/(2c_v)]\mathbf{k} & 0 \end{pmatrix} \quad , \quad (3.3.13)$$

where  $h$  is the enthalpy per particle. The enthalpy comes in upon evaluating the right-hand side of (3.3.3). In fact, we have used a cross-fluctuation formula connecting the energy density and the pressure tensor [27]

$$\frac{1}{V} \langle [\varepsilon(\mathbf{k})]^* \mathbf{k} \cdot \boldsymbol{\tau}(\mathbf{k}) \rangle = - \left( \frac{\partial p}{\partial \beta} \right)_n \mathbf{k} = \frac{nc_v}{k_B \beta^2} \left( \frac{1}{3} + \frac{k_B}{2c_v} \right) \mathbf{k} . \quad (3.3.14)$$

The eigenvalues of the matrix (3.3.13) are the same as those of (3.3.4), so that the mode frequencies are not modified in order  $k$ . Even in order  $k$  the modes show no damping. As to the amplitudes of the modes, several of them get additional terms in order  $k$ . Instead of (3.3.9) and (3.3.11) we find for the heat mode and the plasmon modes:

$$a_\varepsilon(\mathbf{k}) = \left( \frac{k_B \beta^2}{nc_v} \right)^{1/2} [\varepsilon(\mathbf{k}) - hn(\mathbf{k})] , \quad (3.3.15)$$

$$a_\pm(\mathbf{k}) = \frac{1}{(2n)^{1/2}} \left[ \frac{k_D}{k} n(\mathbf{k}) + \beta \left( \frac{1}{3} + \frac{k_B}{2c_v} \right) \frac{k}{k_D} \varepsilon(\mathbf{k}) \pm \left( \frac{\beta}{m} \right)^{1/2} g_{\parallel}(\mathbf{k}) \right] . \quad (3.3.16)$$

The general structure of the collective modes for the OCP is by now clear. Up to first order in the wavenumber the five modes fall apart in a group of three with a vanishing frequency and a group of two with a finite frequency, namely the plasma frequency. All mode frequencies are real in this order of  $k$ , so that the collective modes seem to be undamped. This is a rather unphysical feature of the results obtained so far.

### 3.4 Mode damping

For systems of neutral particles it is well-known that one has to go to second order in the wavenumber before damping phenomena show up. Only in that order the dissipative character of the heat and the viscous modes become apparent. Likewise, the damping of the sound modes is determined by the second-order contributions in the sound mode frequencies. Clearly, the situation is similar for the OCP. We have to evaluate the second-order terms in the mode frequencies in order to find the damping terms.

In second order of the wavenumber the frequencies are no longer determined by the direct part of the frequency matrix only: the indirect part yields a contribution as well. For the heat mode and the viscous modes the latter is the only part that contributes to the second-order term in the mode frequency.

Let us start by considering the *heat* mode. In second order of the wavenumber its frequency is given by:

$$z_\varepsilon = \frac{1}{V} \left\langle [\bar{a}_\varepsilon(\mathbf{k})]^* LQ \frac{1}{z + QLQ} QL a_\varepsilon(\mathbf{k}) \right\rangle . \quad (3.4.1)$$

Inserting (3.3.15) and using the energy balance equation (3.1.15) we find:

$$z_\varepsilon = \frac{k_B \beta^2}{nc_v} k^2 \lim_{\mathbf{k} \rightarrow \mathbf{0}} \frac{1}{V} \left\langle [j_{\varepsilon, \parallel}(\mathbf{k})]^* Q \frac{1}{z + QLQ} Q j_{\varepsilon, \parallel}(\mathbf{k}) \right\rangle . \quad (3.4.2)$$

The right-hand side still depends on  $z$ . Since we are solving for  $z$  in increasing order of the wavenumber, we have to substitute here the frequency in order  $k^0$ . Taking account of the fact that the right-hand side is defined for  $\text{Im } z > 0$  only, we let  $z$  go to 0 along the imaginary axis (and write this limit as  $z \rightarrow i0$ ). In this way we end up with a heat mode frequency of the form:

$$z_\varepsilon = -i \frac{\lambda}{nc_v} k^2 \quad , \quad (3.4.3)$$

with the abbreviation:

$$\lambda = ik_B \beta^2 \lim_{z \rightarrow i0} \lim_{\mathbf{k} \rightarrow \mathbf{0}} \frac{1}{V} \left\langle \left[ j_{\varepsilon, \parallel}(\mathbf{k}) \right]^* Q \frac{1}{z + QLQ} Q j_{\varepsilon, \parallel}(\mathbf{k}) \right\rangle \quad . \quad (3.4.4)$$

We have written  $z_\varepsilon$  in the way of (3.4.3) in order to bring it in the same form as is found from a macroscopic calculation with the help of hydrodynamics [32]. In that theory  $\lambda$  is the (macroscopic) *heat conductivity*. Thus, the expression at the right-hand side of (3.4.4), which can be shown to be real, represents the heat conductivity in the present microscopic theory. Since  $\lambda$  is real, the mode frequency is purely imaginary. The mode decays exponentially fast (in this order of  $k$ ) with a time constant that is proportional to the heat conductivity. The dissipative mechanism that is responsible for the steady decay of the heat mode is the heat conductivity process. Incidentally, it may be remarked that in a fluid of neutral particles a similar heat mode is found, with a mode frequency that differs from (3.4.3) by a factor  $c_p$  instead of  $c_v$  in the denominator.

The formula (3.4.4) for the heat conductivity  $\lambda$  is equivalent to a Green-Kubo expression. In fact, one may prove [29], [31] from (3.4.4):

$$\lambda = k_B \beta^2 \lim_{z \rightarrow i0} \int_0^\infty dt e^{izt} F_\lambda(t) \quad , \quad (3.4.5)$$

with the time correlation function:

$$F_\lambda(t) = \lim_{\mathbf{k} \rightarrow \mathbf{0}} \frac{1}{V} \left\langle \left[ \tilde{j}_{\varepsilon, \parallel}(\mathbf{k}) \right]^* e^{iLt} \tilde{j}_{\varepsilon, \parallel}(\mathbf{k}) \right\rangle \quad . \quad (3.4.6)$$

As in (3.4.4) a projected energy current shows up here. It is defined as:

$$\tilde{j}_{\varepsilon, \parallel}(\mathbf{k}) = Q j_{\varepsilon, \parallel}(\mathbf{k}) = j_{\varepsilon, \parallel}(\mathbf{k}) - \frac{h}{m} g_{\parallel}(\mathbf{k}) \quad . \quad (3.4.7)$$

The derivation of the second-order terms in the mode frequency of the *viscous* modes proceeds in an entirely similar way. We only give the final answer here. The mode frequency in order  $k^2$  has the form:

$$z_\eta = -i \frac{\eta}{nm} k^2 \quad , \quad (3.4.8)$$

with the *viscosity coefficient*:

$$\eta = i\beta \lim_{z \rightarrow i0} \lim_{\mathbf{k} \rightarrow \mathbf{0}} \frac{1}{V} \left\langle \left[ \tau_{\parallel, \perp}(\mathbf{k}) \right]^* Q \frac{1}{z + QLQ} Q \tau_{\parallel, \perp}(\mathbf{k}) \right\rangle \quad . \quad (3.4.9)$$

Once again, the frequency is purely imaginary. The damping mechanism is viscous flow.

Finally, we turn to the *plasmon* modes. Here, both the direct and the indirect part of the frequency matrix contribute to the second-order terms in the mode frequency. Employing a perturbation type of approach to evaluate these terms one finds up to second order in  $k$ :

$$z_{\pm} = \pm\omega_p \left( 1 + \frac{c_s^2}{2\omega_p^2} k^2 \right) - i \frac{\gamma_{\pm}}{2nm} k^2 \quad . \quad (3.4.10)$$

Here  $c_s$  is the “sound velocity” which is formally defined by the same combination of thermodynamic derivatives as for a system of neutral particles:

$$c_s^2 = \frac{c_p}{c_v} \frac{1}{nm\kappa_T} \quad . \quad (3.4.11)$$

[This velocity has a formal meaning only for the OCP, since sound propagation is not possible in this system.] The last term in (3.4.10) has arisen from the indirect part of the frequency matrix. It has the form:

$$\gamma_{\pm} = i\beta \lim_{z \rightarrow \pm\omega_p} \lim_{\mathbf{k} \rightarrow \mathbf{0}} \frac{1}{V} \left\langle \left[ \tau_{\parallel, \parallel}(\mathbf{k}) \right]^* Q \frac{1}{z + QLQ} Q \tau_{\parallel, \parallel}(\mathbf{k}) \right\rangle \quad . \quad (3.4.12)$$

As before the frequency  $z$  in the denominator at the right-hand side has been replaced by the zeroth-order mode frequency of the plasmon modes. Since the latter differs from zero,  $\gamma$  is complex, so that the last term of (3.4.10) leads both to damping (due to the real part of  $\gamma$ ) and to dispersion (due to the imaginary part of  $\gamma$ ). One may prove  $[\gamma_{\pm}]^* = \gamma_{\mp}$ , so that the two plasmon modes have equal damping rates but opposite dispersion. Neither the damping nor the dispersion is determined by a *static* transport coefficient, as it was the case for the heat mode and the viscous modes. Instead, a *dynamical* coefficient at a finite frequency (namely  $\omega_p$ ) shows up. Apart from this feature its form is closely analogous to (3.4.9). One may thus say that the damping (and the dispersion) of the plasmon modes is determined by a dynamical viscosity coefficient. A detailed comparison with hydrodynamics shows that the precise combination of viscosity coefficients is  $(4/3)\eta(z) + \eta_v(z)$ , with  $\eta_v$  the volume viscosity, so that one has:

$$\gamma_{\pm} = \frac{4}{3}\eta(\pm\omega_p) + \eta_v(\pm\omega_p) \equiv \frac{4}{3}\eta_{\pm} + \eta_{v, \pm} \quad . \quad (3.4.13)$$

In conclusion, we have seen that in the OCP five collective modes can be sustained. Some of these, namely the heat mode and the viscous modes, are rather similar to those found in a fluid of neutral particles, as can be seen from table 3.1. A qualitatively different behaviour is found, however, for the remaining two modes: instead of the usual sound modes one finds two plasmon modes. These are oscillating modes with a basic frequency given by the plasma frequency. The damping of these plasmon modes turns out to be governed by a dynamical (finite-frequency) viscosity coefficient.

neutral fluid	OCP
heat mode $z_\varepsilon = -i \frac{\lambda}{nc_p} k^2$	heat mode $z_\varepsilon = -i \frac{\lambda}{nc_v} k^2$
viscous modes $z_\eta = -i \frac{\eta}{nm} k^2$	viscous modes $z_\eta = -i \frac{\eta}{nm} k^2$
sound modes $z_\pm = \pm c_s k - i \frac{1}{2nm} \left( \frac{4}{3} \eta + \eta_v \right) k^2$ $-i \frac{\lambda}{2n} \left( \frac{1}{c_v} - \frac{1}{c_p} \right) k^2$	plasmon modes $z_\pm = \pm \omega_p \left( 1 + \frac{c_s^2}{2\omega_p^2} k^2 \right)$ $-i \frac{1}{2nm} \left( \frac{4}{3} \eta_\pm + \eta_{v,\pm} \right) k^2$

Table 3.1: Collective mode frequencies of a fluid of neutral particles and of the OCP.

## Hoofdstuk 4

# Time correlation functions

### 4.1 Velocity autocorrelation function

In the previous chapter we have encountered an example of a Green-Kubo relation for a transport coefficient, viz. (3.4.5) for the heat conductivity. Quite generally a Green-Kubo relation yields an expression for a transport coefficient in the form of an integral over a time correlation function. As (3.4.6) shows, the relevant time correlation function that shows up in the heat conductivity describes the correlations of the (projected) energy current at different times.

Intuitively one expects that for large values of the elapsed time  $t$  the correlations in the system will disappear rapidly. Correspondingly, the time correlation functions are expected to decay fast towards zero, thus ensuring the rapid convergence of the Green-Kubo integrals in the limit  $z \rightarrow i0$ . For a long time people have tacitly assumed without proof that the decay of the time correlation functions would be exponentially fast. Hence, it came as a great surprise, when some twenty years ago [33] molecular dynamics calculations indicated that the decay of the time correlation functions for fluids is usually governed by an algebraic rather than an exponential dependence on  $t$ .

In the following we shall discuss the long-time behaviour of the time correlation functions for the OCP. It will be found that the presence of plasmons in the OCP has a profound influence on this behaviour. To simplify matters we shall, for most of the time, confine ourselves to a particular case, namely the time correlation function that occurs in the Green-Kubo integral for the self-diffusion.

As is well-known, diffusion of a tagged particle through a fluid (or an OCP) is described by the coefficient of self-diffusion  $D_s$  that is defined by the ratio of the averaged square of the particle displacement and the elapsed time. Writing the position vector of the particle at time  $t$  as  $\mathbf{r}_s(t)$  we have:

$$D_s = \lim_{t \rightarrow \infty} \frac{1}{6t} \langle |\mathbf{r}_s(t) - \mathbf{r}_s(0)|^2 \rangle \quad . \quad (4.1.1)$$

Introducing the momentum  $\mathbf{p}_s(t)$  of the tagged particle we may write:

$$\mathbf{r}_s(t) - \mathbf{r}_s(0) = \frac{1}{m} \int_0^t dt' \mathbf{p}_s(t') \quad , \quad (4.1.2)$$

and hence:

$$\begin{aligned}
& \left\langle | \mathbf{r}_s(t) - \mathbf{r}_s(0) |^2 \right\rangle = \\
&= \frac{1}{m^2} \int_0^t dt' \int_0^t dt'' \langle \mathbf{p}_s(t') \cdot \mathbf{p}_s(t'') \rangle = \\
&= \frac{2}{m^2} \int_0^t d\tau (t - \tau) \langle \mathbf{p}_s(\tau) \cdot \mathbf{p}_s(0) \rangle \quad , \quad (4.1.3)
\end{aligned}$$

where we used the time translation invariance of the time correlation function. Combining (4.1.1) and (4.1.3) we get:

$$D_s = \frac{1}{3m^2} \int_0^\infty d\tau \langle \mathbf{p}_s(\tau) \cdot \mathbf{p}_s(0) \rangle \quad , \quad (4.1.4)$$

where we have assumed that the integral converges. This result is the simplest example of a Green-Kubo relation for a transport coefficient. Usually one introduces the *velocity autocorrelation function*:

$$F(t) = \frac{1}{3m^2} \langle \mathbf{p}_s(t) \cdot \mathbf{p}_s(0) \rangle = \frac{1}{3} \langle \mathbf{v}_s(t) \cdot \mathbf{v}_s(0) \rangle \quad , \quad (4.1.5)$$

with  $\mathbf{v}(t)$  the tagged-particle velocity at time  $t$ . Then the diffusion coefficient gets the simple form:

$$D_s = \int_0^\infty dt F(t) \quad . \quad (4.1.6)$$

A form for  $D_s$  that resembles (3.4.5) even more closely is found by introducing the tagged-particle momentum density in Fourier space:

$$\mathbf{g}_s(\mathbf{k}) = \mathbf{p}_s e^{-i\mathbf{k}\cdot\mathbf{r}_s} \quad . \quad (4.1.7)$$

Then we may write (4.1.4) in the form:

$$D_s = \frac{1}{3nm^2} \lim_{z \rightarrow i0} \int_0^\infty dt e^{izt} F_s(t) \quad , \quad (4.1.8)$$

with the time correlation function:

$$F_s(t) = \lim_{\mathbf{k} \rightarrow \mathbf{0}} \frac{1}{V} \left\langle \left[ \sqrt{N} \mathbf{g}_s(\mathbf{k}) \right]^* \cdot e^{iLt} \sqrt{N} \mathbf{g}_s(\mathbf{k}) \right\rangle \quad , \quad (4.1.9)$$

where we added factors  $\sqrt{N}$  in order to get a finite answer in the thermodynamic limit. Performing the time integral in (4.1.8) we get the relation:

$$D_s = \frac{i}{3nm^2} \lim_{z \rightarrow i0} \lim_{\mathbf{k} \rightarrow \mathbf{0}} \frac{1}{V} \left\langle \left[ \sqrt{N} \mathbf{g}_s(\mathbf{k}) \right]^* \cdot \frac{1}{z + L} \sqrt{N} \mathbf{g}_s(\mathbf{k}) \right\rangle \quad . \quad (4.1.10)$$

An alternative method to arrive at this result starts from the conserved quantities for the tagged-particle motion. In fact, we have only one such conserved quantity, viz. the tagged-particle density:

$$n_s(\mathbf{k}) = e^{-i\mathbf{k}\cdot\mathbf{r}_s} \quad , \quad (4.1.11)$$



for which the conservation law is:

$$iLn_s(\mathbf{k}) = -i\mathbf{k} \cdot \frac{\mathbf{g}_s(\mathbf{k})}{m} \quad . \quad (4.1.12)$$

The fluctuation formula for the tagged-particle density is easily seen to be:

$$\frac{1}{V} \left\langle \left[ \sqrt{N}n_s(\mathbf{k}) \right]^* \sqrt{N}n_s(\mathbf{k}) \right\rangle = n \quad , \quad (4.1.13)$$

where we inserted factors  $\sqrt{N}$ , as before. We now define a projection operator  $P_s$  that projects onto the (one-dimensional) space spanned by the basis function

$$a_s(\mathbf{k}) = \frac{1}{\sqrt{n}} \sqrt{N}n_s(\mathbf{k}) \quad . \quad (4.1.14)$$

The factor  $\sqrt{n}$  is chosen such that the adjoint  $\bar{a}_s(\mathbf{k})$  coincides with  $a_s(\mathbf{k})$ . The propagator

$$G_s(\mathbf{k}, z) = \frac{1}{V} \left\langle [\bar{a}_s(\mathbf{k})]^* \frac{1}{z+L} a_s(\mathbf{k}) \right\rangle \quad (4.1.15)$$

satisfies an equation analogous to (3.2.13):

$$(z - \Omega)G_s = 1 \quad , \quad (4.1.16)$$

with  $\Omega$  the sum of a direct and an indirect part. These are given by:

$$\Omega^{dir}(\mathbf{k}, z) = -\frac{1}{V} \left\langle [\bar{a}_s(\mathbf{k})]^* L a_s(\mathbf{k}) \right\rangle \quad , \quad (4.1.17)$$

$$\Omega^{ind}(\mathbf{k}, z) = \frac{1}{V} \left\langle [\bar{a}_s(\mathbf{k})]^* L Q_s \frac{1}{z + Q_s L Q_s} Q_s L a_s(\mathbf{k}) \right\rangle \quad . \quad (4.1.18)$$

Obviously, the direct part vanishes identically, while the indirect part is of second order in the wavenumber. Hence, the tagged-particle mode frequency  $z_s$  is zero in leading order of  $k$ . In order  $k^2$  we find:

$$z_s = \frac{1}{nm^2} k^2 \lim_{\mathbf{k} \rightarrow \mathbf{0}} \frac{1}{V} \left\langle \left[ \sqrt{N}g_{s,\parallel}(\mathbf{k}) \right]^* Q_s \frac{1}{z + Q_s L Q_s} Q_s \sqrt{N}g_{s,\parallel}(\mathbf{k}) \right\rangle \quad . \quad (4.1.19)$$

Using the isotropy of the system and inserting for  $z$  the zeroth-order frequency we finally get:

$$z_s = -ik^2 D_s \quad , \quad (4.1.20)$$

with the self-diffusion coefficient:

$$D_s = \frac{i}{3nm^2} \lim_{z \rightarrow i0} \lim_{\mathbf{k} \rightarrow \mathbf{0}} \frac{1}{V} \left\langle \left[ \sqrt{N}\mathbf{g}_s(\mathbf{k}) \right]^* \cdot Q_s \frac{1}{z + Q_s L Q_s} Q_s \sqrt{N}\mathbf{g}_s(\mathbf{k}) \right\rangle \quad . \quad (4.1.21)$$

This result is equivalent to (4.1.10), since the two averages at the right-hand sides of (4.1.10) and (4.1.21) coincide in the limit  $\mathbf{k} \rightarrow \mathbf{0}$ . The (normalized) mode amplitude of the tagged-particle mode is given by (4.1.14).

## 4.2 Long-time behaviour of the velocity autocorrelation function

We are interested in the decay of time-dependent correlations as described by the velocity autocorrelation function. Instead of  $F(t)$  we prefer to study the equivalent time correlation function  $F_s(t)$  defined in (4.1.9).

In the previous chapter we have studied the collective modes in the OCP. We have seen that in the long-wavelength limit these modes are undamped. Their damping is governed by terms that are of order  $k^2$ . The reason for the slow damping of the modes is clear: they cannot decay swiftly, since they are linear combinations of quantities [viz.  $n(\mathbf{k})$ ,  $\mathbf{g}(\mathbf{k})$  and  $\varepsilon(\mathbf{k})$ ] that are conserved in the long-wavelength limit. As the modes exhaust all possible linear combinations of the conserved quantities, one expects that quite generally slow decay of a time-dependent quantity must be connected to the modes. It must be noted, however, that one need not confine oneself to linear combinations: any nonlinear combination of the conserved quantities, or of the modes, might equally well contribute to the mechanism of slow decay in a particular case. For instance, a product of two mode amplitudes has a slow decay as well, at least in the long-wavelength limit. With these remarks in mind we return to the particular subject of our present interest: the velocity autocorrelation function in its form (4.1.9).

We start by writing (4.1.9) in a slightly different form, by introducing the projection operator  $Q_s$ :

$$F_s(t) = \lim_{\mathbf{k} \rightarrow \mathbf{0}} \frac{1}{V} \left\langle \left[ \sqrt{N} \mathbf{g}_s(\mathbf{k}) \right]^* Q_s \cdot e^{iLt} Q_s \sqrt{N} \mathbf{g}_s(\mathbf{k}) \right\rangle , \quad (4.2.1)$$

This is a trivial step since  $P_s \mathbf{g}_s(\mathbf{k})$  vanishes. The reason for doing this is that we now see that the long-time behaviour of  $F_s(t)$  can not be governed simply by the relevant tagged-particle mode  $a_s(\mathbf{k})$ , although the latter decays slowly. In fact, the projection operator  $Q_s$  projects “away” from  $a_s(\mathbf{k})$ . The five collective modes  $a_i(\mathbf{k})$  for the OCP as a whole can not contribute either, since they would lead to expressions of the form:

$$\frac{1}{V} \left\langle \left[ \sqrt{N} \mathbf{g}_s(\mathbf{k}) \right]^* a_i(\mathbf{k}) \right\rangle \cdot \frac{1}{V} \left\langle [a_i(\mathbf{k})]^* e^{iLt} \sqrt{N} \mathbf{g}_s(\mathbf{k}) \right\rangle , \quad (4.2.2)$$

which vanish in the thermodynamic limit.

We thus have to resort to nonlinear combinations of the tagged-particle mode  $a_s(\mathbf{k})$  and the collective modes  $a_i(\mathbf{k})$ . The simplest nonlinear combinations are products of two of these. In the thermodynamic limit only products of the tagged-particle mode with one of the collective modes survive. In constructing these products one should allow modes with different wavevector, chosen such that the wavevectors add up to  $\mathbf{k}$ . The mode products evolve in time as:

$$e^{iLt} a_s(\mathbf{q}) a_i(\mathbf{k} - \mathbf{q}) = e^{-i[z_s(\mathbf{q}) + z_i(\mathbf{k} - \mathbf{q})]t} , \quad (4.2.3)$$

in leading order of the wavenumbers. On the basis of (4.2.1) we arrive at the following expression:

$$\lim_{\mathbf{k} \rightarrow \mathbf{0}} \sum_{i=1}^5 \int \frac{d\mathbf{q}}{(2\pi)^3} | \mathbf{A}_i(\mathbf{k}, \mathbf{q}) |^2 e^{-i[z_s(\mathbf{q}) + z_i(\mathbf{k} - \mathbf{q})]t} , \quad (4.2.4)$$

with the coefficients:

$$\mathbf{A}_i(\mathbf{k}, \mathbf{q}) = \frac{1}{V} \left\langle [a_s(\mathbf{q})a_i(\mathbf{k} - \mathbf{q})]^* \sqrt{N} \mathbf{g}_s(\mathbf{k}) \right\rangle . \quad (4.2.5)$$

In this expression the two modes (the tagged-particle mode  $a_s$  and the collective mode  $a_i$ ) are “coupled” to the central quantity  $\mathbf{g}_s$ . Correspondingly, the expression (4.2.4) is called a *mode-coupling* expression; the amplitudes  $\mathbf{A}_i$  are called the “*mode-coupling amplitudes*”. The theory of mode coupling (or *mode-mode coupling*) has been invented to describe dynamical effects near phase transitions [34] – [36]. Later on it has been realized [37] that mode-coupling theory could be used as well to obtain the long-time behaviour of time correlation functions. Indeed, it has been proved that the dominant contribution in the asymptotic behaviour is given by the term with a product of two modes only. Higher-order terms can be neglected in the limit of large  $t$ . Hence, the mode-coupling expression (4.2.4) represents the asymptotic form of  $F_s(t)$  for large  $t$ .

Before evaluating (4.2.4) we note that the main contribution in the integral comes from small  $\mathbf{q}$ , since the damping terms in the exponential function effectively destroy the contributions of high  $\mathbf{q}$ . In working out the amplitudes we thus need to consider only the leading terms for small  $\mathbf{k}$  and  $\mathbf{q}$ . Inserting  $a_s$  and  $\mathbf{g}_s$  in (4.2.5) we get:

$$\mathbf{A}_i(\mathbf{k}, \mathbf{q}) = \frac{1}{n^{1/2}} \frac{1}{V} \left\langle [a_i(\mathbf{k} - \mathbf{q})]^* N \mathbf{p}_s e^{-i(\mathbf{k} - \mathbf{q}) \cdot \mathbf{r}_s} \right\rangle . \quad (4.2.6)$$

The mode amplitudes differ from zero only if the collective modes  $a_i$  contain a term with the momentum density, since the average of an odd number of momenta vanishes. Hence, only the viscous modes (3.3.8) and the plasmon modes (3.3.11) (or (3.3.16) in first order) contribute. Evaluating the averages we find for the amplitudes:

$$\mathbf{A}_{\perp,i} = \left( \frac{m}{\beta} \right)^{1/2} \mathbf{e}_{\perp,i} , \quad (4.2.7)$$

$$\mathbf{A}_{\pm} = \pm \left( \frac{m}{2\beta} \right)^{1/2} \hat{\mathbf{q}} , \quad (4.2.8)$$

with  $\mathbf{e}_{\perp,i}$  (for  $i = 1, 2$ ) unit vectors orthogonal to the wavevector  $\mathbf{q}$ .

Inserting the mode amplitudes in (4.2.4) and substituting moreover the mode frequencies (4.1.20), (3.4.8) and (3.4.10) we arrive at the asymptotic expression:

$$F_s(t) \simeq \frac{m}{\beta} \int \frac{d\mathbf{q}}{(2\pi)^3} \left[ 2 \exp \left[ -i \left( -iD_s q^2 - i \frac{\eta}{nm} q^2 \right) t \right] + \frac{1}{2} \sum_{\pm} \exp \left\{ -i \left[ -iD_s q^2 \pm \omega_p \left( 1 + \frac{c_s^2}{2\omega_p^2} q^2 \right) - i \frac{\gamma_{\pm}}{2nm} q^2 \right] t \right\} \right] . \quad (4.2.9)$$

The integrals can be evaluated with the help of the identity:

$$\int_0^{\infty} dq q^{2n} e^{-aq^2} = \sqrt{\pi} \frac{(2n)!}{n!} \frac{1}{(4a)^{n+1/2}} , \quad (4.2.10)$$

valid for any complex  $a$  with a positive real part and for any integer  $n > 0$ . Using this identity we finally get for the asymptotic behaviour of  $F_s(t)$ :

$$F_s(t) \simeq \frac{m}{\beta} \left[ A + B \cos \left( \omega_p t + \frac{3}{2} \theta \right) \right] \frac{1}{(4\pi t)^{3/2}} \quad . \quad (4.2.11)$$

Here we used the abbreviations:

$$A = 2 \left( D_s + \frac{\eta}{nm} \right)^{-3/2} \quad , \quad (4.2.12)$$

$$B = \left[ \left( D_s + \frac{\gamma'}{2nm} \right)^2 + \left( \frac{c_s^2}{2\omega_p} + \frac{\gamma''}{2nm} \right)^2 \right]^{-3/4} \quad , \quad (4.2.13)$$

with  $\gamma' = \text{Re } \gamma_+$  and  $\gamma'' = \text{Im } \gamma_+$ . Furthermore we defined the angle:

$$\theta = \arctan \left[ \left( \frac{c_s^2}{2\omega_p} + \frac{\gamma''}{2nm} \right) / \left( D_s + \frac{\gamma'}{2nm} \right) \right] \quad . \quad (4.2.14)$$

As can be seen from (4.2.11) the time correlation function  $F_s(t)$ , and hence also the velocity autocorrelation function  $F(t)$  for a tagged particle in an OCP, have a slowly decaying tail proportional to  $t^{-3/2}$ . A similar tail has been found previously for a tagged particle in a neutral fluid [33]. However, for an OCP part of the tail is modulated by a cosine that oscillates at the plasma frequency. This oscillating behaviour of the velocity autocorrelation function has indeed been found in molecular dynamics calculations [38].

### 4.3 Outlook

In this final section we shall discuss a few topics in the statistical theory of Coulomb systems that are closely related to the subjects treated above and for which new results have been obtained recently. These are:

- sum rules and fluctuation formulas for ionic mixtures;
- collective modes for an OCP embedded in a magnetic field;
- long-time tails of the velocity autocorrelation function for a tagged particle in a magnetized OCP;
- long-time tails for Green-Kubo integrands of the heat conductivity and the viscosity.

**Sum rules and fluctuation formulas for ionic mixtures.** An ionic mixture consists of particles of several species that move in an inert neutralizing background. The charges and masses of the particles differ from one species to the other; they are written as  $e_\sigma$  and  $m_\sigma$ , respectively, with  $\sigma$  labelling the species. The background charge density is written as  $-q_v$ . The system is neutral if the particle numbers  $N_\sigma$

of the various species satisfy the relation  $\sum_{\sigma} e_{\sigma} N_{\sigma} = q_v V$ . A description of an ionic mixture in equilibrium can be given with an ensemble that is closely analogous to the canonical ensemble for the OCP, namely a grand-canonical ensemble in which the particles numbers are restricted so as to guarantee charge neutrality [18]. Alternatively, one may use a fully unrestricted grand-canonical ensemble with a fixed background charge density [39].

By using similar techniques as given above for the OCP one may establish sum rules for the partial Ursell functions  $h_{\sigma_1, \sigma_2}^{(2)}(r)$  of the ionic mixture. The analogue of the perfect-screening sum rule has the form:

$$\sum_{\sigma_2} n_{\sigma_2} e_{\sigma_2} \int d\mathbf{r} h_{\sigma_1, \sigma_2}^{(2)}(r) = -e_{\sigma_1} \quad . \quad (4.3.1)$$

One should note the sum over species occurring at the left-hand side: a charge at the origin is compensated by charges elsewhere in the system only, if all species are taken into account. One may derive a sum rule for the partial Ursell function by itself (without a sum over species), but that sum rule contains thermodynamic derivatives that can not be evaluated easily:

$$n_{\sigma_1} n_{\sigma_2} \int d\mathbf{r} h_{\sigma_1, \sigma_2}^{(2)}(r) = \beta^{-1} \left( \frac{\partial n_{\sigma_1}}{\partial \mu_{\sigma_2}} - \frac{1}{S} \frac{\partial q_v}{\partial \mu_{\sigma_1}} \frac{\partial q_v}{\partial \mu_{\sigma_2}} \right) - n_{\sigma_1} \delta_{\sigma_1, \sigma_2} \quad , \quad (4.3.2)$$

with  $\mu_{\sigma}$  the thermodynamical potential of component  $\sigma$  and  $S$  standing for the abbreviation  $\sum_{\sigma} e_{\sigma} \partial q_v / \partial \mu_{\sigma}$ . The analogue of the Stillinger-Lovett relation is:

$$\sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1} e_{\sigma_2} \int d\mathbf{r} r^2 h_{\sigma_1, \sigma_2}^{(2)}(r) = -\frac{6}{\beta} \quad . \quad (4.3.3)$$

Here a summation over both species, with appropriate weights, is needed to produce a simple answer. No general result is available for the second moment of a separate partial Ursell function (without a sum over species). Finally, a fourth-moment sum rule can be proved for the ionic mixture as well:

$$\sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1} e_{\sigma_2} \int d\mathbf{r} r^4 h_{\sigma_1, \sigma_2}^{(2)}(r) = -\frac{120}{\beta S} \quad . \quad (4.3.4)$$

Again, a sum rule for the separate Ursell function does not exist.

The sum rules can be used to derive fluctuation formulas for the ionic mixture. It turns out that the fluctuation formula for the partial density  $n_{\sigma}(\mathbf{k})$  in Fourier space starts with a term of order  $k^0$ , as follows from (4.3.2). On the other hand, the charge density fluctuation formula, which describes the behaviour of  $q_v(\mathbf{k}) = \sum_{\sigma} e_{\sigma} n_{\sigma}(\mathbf{k})$  for large wavelength, starts with a term of order  $k^2$ :

$$\frac{1}{V} \langle [q_v(\mathbf{k})]^* q_v(\mathbf{k}) \rangle = \beta^{-1} k^2 + \dots \quad . \quad (4.3.5)$$

Thus, fluctuations in the total density  $n(\mathbf{k}) = \sum_{\sigma} n_{\sigma}(\mathbf{k})$  may occur in the long-wavelength limit, whereas fluctuations in the charge density are suppressed as in the OCP.

**Collective modes for an OCP embedded in a magnetic field.** In nature Coulomb systems are often situated in a magnetic field. In such a situation the charged particles feel, apart from their mutual Coulomb forces, the Lorentz force generated by the magnetic field. The simplest configuration that can be imagined to study the influence of magnetic fields on the properties of Coulomb systems is that of a uniform time-independent magnetic field. The presence of such a magnetic field does not change the equilibrium properties of a classical charged particle system, as follows from the theorem by Bohr and van Leeuwen. On the other hand, the dynamical properties will change. In particular, one may ask how the collective mode spectrum is modified by the external field.

The collective modes for an OCP in a magnetic field can be found with the same method as described in chapter 3, although the analysis is considerably more complex [29]. Most complications arise from the fact that the spherical symmetry of the unmagnetized OCP is reduced to a cylinder symmetry around the direction of the magnetic field. The modes now depend on two vectors, namely the wavevector  $\mathbf{k}$  and a unit vector  $\hat{\mathbf{B}}$  pointing in the direction of the field. As a consequence the viscous modes are no longer decoupled. They merge with the plasmon modes into a set of four new field-dependent modes, the so-called *gyroplasmon modes*. In zeroth order of the wavenumber the frequencies of these new modes are given by the expressions:

$$z_{\lambda,\rho} = \rho w_\lambda \quad (\lambda = \pm 1, \rho = \pm 1) \quad , \quad (4.3.6)$$

Here  $w_\lambda$  is given by:

$$w_\lambda = \frac{1}{2} \left( \omega_p^2 + \omega_B^2 + 2\omega_p\omega_B\hat{k}_\parallel \right)^{1/2} + \frac{1}{2}\lambda \left( \omega_p^2 + \omega_B^2 - 2\omega_p\omega_B\hat{k}_\parallel \right)^{1/2} \quad , \quad (4.3.7)$$

where  $\hat{k}_\parallel$  stands for  $\hat{\mathbf{k}} \cdot \hat{\mathbf{B}}$ . Furthermore,  $\omega_B$  is the cyclotron frequency  $eB/(mc)$ , which is a measure of the strength of the magnetic field. In second order of the wavenumber damping terms show up in the frequencies of the gyroplasmon modes. These damping terms depend on the dynamical viscosity coefficients of the magnetized OCP at a frequency given by (4.3.6). Owing to the presence of the magnetic field the number of independent viscosity coefficients is *seven*, namely five transverse viscosity coefficients  $\eta_1, \dots, \eta_5$ , one volume viscosity coefficient  $\eta_v$  and one mixed coefficient  $\zeta$ . All these contribute to the damping.

The gyroplasmon mode amplitudes in leading order of the wavevector also show the anisotropy introduced by the magnetic field. In fact, one finds:

$$a_{\lambda,\rho}(\mathbf{k}) = C_\lambda \left[ \frac{k_D}{k} n(\mathbf{k}) + \left( \frac{\beta}{m} \right)^{1/2} \mathbf{v}_{\lambda,\rho}(\hat{\mathbf{k}}) \cdot \mathbf{g}(\mathbf{k}) \right] \quad , \quad (4.3.8)$$

with  $C_\lambda$  a normalization factor and  $\mathbf{v}_{\lambda,\rho}(\hat{\mathbf{k}})$  a vector depending on the unit vector  $\hat{\mathbf{k}}$  and its components parallel and perpendicular to the magnetic field  $\hat{\mathbf{k}}_\parallel = \hat{k}_\parallel \hat{\mathbf{B}}$  and  $\hat{\mathbf{k}}_\perp = \hat{\mathbf{k}} - \hat{\mathbf{k}}_\parallel$ :

$$\mathbf{v}_{\lambda,\rho}(\hat{\mathbf{k}}) = \frac{\rho w_\lambda \omega_p}{w_\lambda^2 - \omega_B^2} \hat{\mathbf{k}}_\perp + \frac{\rho \omega_p}{w_\lambda \hat{k}_\parallel} \hat{\mathbf{k}}_\parallel - \frac{i \omega_p \omega_B}{w_\lambda^2 - \omega_B^2} \hat{\mathbf{k}} \wedge \hat{\mathbf{B}} \quad . \quad (4.3.9)$$

The fifth mode of the magnetized OCP is the heat mode, as before. Its damping coefficient is now governed by *two* independent heat conductivity coefficients associated to heat conduction parallel and perpendicular to the field.

**Long-time tails of the velocity autocorrelation function for a tagged particle in a magnetized OCP.** As we have seen the velocity autocorrelation function for a tagged particle that moves through an OCP is determined by the coupling of the particle momentum to the viscous modes and to the plasmon modes. As a consequence the autocorrelation function is the sum of two terms, one decaying proportional to  $t^{-3/2}$  and the other proportional to  $t^{-3/2} \cos(\omega_p t + \theta)$ . In a magnetized OCP these modes are no longer present. One expects instead that the tagged-particle momentum is coupled now to the gyroplasmon modes. Indeed, this turns out to be the case. However, these gyroplasmon modes are orientation-dependent. In particular, their frequencies depend on the angle between the wavevector and the magnetic field. Since the mode-coupling expression for the asymptotic autocorrelation function contains an integral over all wavevectors of the modes, contributions with different frequencies from a whole frequency range must be added together. Clearly, this addition will give rise to interference effects that may change the long-time behaviour quite drastically. A detailed calculation [40] confirms these expectations. The long-time tail of the velocity autocorrelation function is found to be different for the velocity components parallel and transverse to the magnetic field. Both tails are decaying algebraically, but with a different exponent. Moreover, both are oscillating, but with different oscillation frequencies. The results are:

$$F_{\parallel}(t) \propto t^{-5/2} \cos(\omega_p t + \theta_{\parallel}) \quad , \quad (4.3.10)$$

$$F_{\perp}(t) \propto t^{-2} \cos(\omega_0 t + \theta_{\perp}) \quad , \quad (4.3.11)$$

where we have omitted proportionality constants for which explicit expressions are available [40]. The oscillating frequency of the parallel-velocity autocorrelation function is the plasma frequency, as before. The influence of the magnetic field appears only through the algebraic factor the exponent of which has changed from  $-3/2$  to  $-5/2$ . In contrast, in the autocorrelation function for the transverse velocity the presence of the magnetic field is felt not only in the algebraic factor, of which the exponent is changed to  $-2$ , but also in the oscillation frequency, which is now  $\omega_0 \equiv (\omega_p^2 + \omega_B^2)^{1/2}$ . The importance of this “composite” frequency in the dynamics of a magnetized OCP has been confirmed in molecular dynamics calculations [41].

**Long-time tails for Green-Kubo integrands of the heat conductivity and the viscosity.** As a final item we shortly discuss the long-time tails of the time correlation functions for the (projected) energy current and pressure tensor that appear in the integrands of the Green-Kubo expressions for the heat conductivity and the viscosity coefficient. Recently, these tails have been evaluated with the help of mode-coupling theory, both for the unmagnetized and the magnetized OCP [28], [42]. For both cases it has been found that the viscosity Green-Kubo integrand behaves more or less in a similar way as the velocity autocorrelation function, with oscillating terms for the unmagnetized OCP and interference effects in the magnetized OCP.

The situation is different, however, for the Green-Kubo integrand that determines the heat conductivity. The latter is found to decay rather more slowly, viz. proportional to  $t^{-1/2}$ . For the unmagnetized OCP this tail is modulated by a goniometric factor, whereas for the magnetized OCP the dominant contribution to the tail does not contain any such factor: it is simply given by  $t^{-1/2}$ . This last result is rather disconcerting, as it means that upon integration of the Green-Kubo integrand an *infinite* result is found for the static heat conductivity of a magnetized OCP. It has been proved recently [43] that this is a peculiarity of the OCP. In a (magnetized) ionic mixture no such singularity is found, at least if the mixture contains species of particles with a different ratio  $e/m$  of charge to mass. Hence, the occurrence of particles with a different  $e/m$  ratio is an essential prerequisite for the validity of dissipative magnetohydrodynamics.



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