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# Electrostatic screening in classical Coulomb fluids: exponential or power-law decay or both? An investigation into the effect of dispersion interactions

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## Abstract

It is shown that the nature of the non-electrostatic part of the pair interaction potential in classical Coulomb fluids can have a profound influence on the screening behaviour. Two cases are compared: (i) when the non-electrostatic part equals an arbitrary finite-ranged interaction and (ii) when a dispersion  $r^{-6}$  interaction potential is included. A formal analysis is done in exact statistical mechanics, including an investigation of the bridge function. It is found that the Coulombic  $r^{-1}$  and the dispersion  $r^{-6}$  potentials are coupled in a very intricate manner as regards the screening behaviour. The classical one-component plasma (OCP) is a particularly clear example due to its simplicity and is investigated in detail. When the dispersion  $r^{-6}$  potential is turned on, the screened electrostatic potential from a particle goes from a monotonic exponential decay,  $\exp(-\kappa r)/r$ , to a power-law decay,  $r^{-8}$ , for large  $r$ . The pair distribution function acquires, at the same time, an  $r^{-10}$  decay for large  $r$  instead of the exponential one. There still remains exponentially decaying contributions to both functions, but these contributions turn oscillatory when the  $r^{-6}$  interaction is switched on. When the Coulomb interaction is turned off but the dispersion  $r^{-6}$  pair potential is kept, the decay of the pair distribution function for large  $r$  goes over from the  $r^{-10}$  to an  $r^{-6}$  behaviour, which is the normal one for fluids of electroneutral particles with dispersion interactions. Differences and similarities compared to binary electrolytes are pointed out.

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## 1. Introduction

When modelling classical Coulomb fluids one usually uses pair interaction potentials that have a finite-ranged part in addition to the Coulombic part, for example the primitive model (PM) for electrolytes which models the ions as charged hard spheres and the solvent as a dielectric continuum. One usually does not include any dispersion interactions despite that such a contribution is always present in real systems such as electrolytes, molten salts, colloidal dispersions and plasmas. This neglect may have important consequences as regards the realism of the model. For example, it has been found for quantum Coulomb fluids [1, 2] that the quantum fluctuations that cause the dispersion interaction also kill the exponential screening ('Debye screening') found in the usual classical models like PM. Instead one finds that the decay of the distribution functions follows power laws in the quantum case. The density–density correlations then have an  $r^{-6}$  decay for large distances  $r$ , the charge–density correlations have an  $r^{-8}$  decay and charge–charge correlations an  $r^{-10}$  decay.

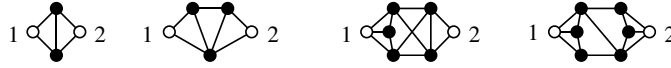
Furthermore, it has quite recently been pointed out by Ninham and Yaminsky [3] that the inclusion of dispersion interactions between charged particles in the treatment of electrostatic interactions in electrolyte systems should have important consequences. Calculations of various properties of electrolyte solutions and colloidal dispersions point in the direction that this is probably correct [4–6].

Note that the question is what happens when the dispersion interaction is included in the pair interaction between *all* particles. This is very different from traditional theories of colloidal interactions, where the van der Waals interaction (including dispersion interaction) between colloidal particles is added to the electrostatic (double layer) free energy of interaction. Then the van der Waals and the double layer interactions between the macroparticles are assumed to be independent and additive as an approximation.

Kjellander and Forsberg [7] recently investigated classical binary electrolytes where an effective  $r^{-6}$  dispersion interaction potential was included in the pair interaction potential between the ions. It was found that the fluid in general have the same  $r^{-6}$ ,  $r^{-8}$  and  $r^{-10}$  decay behaviour as in the quantum case for the density–density, charge–density and charge–charge correlation functions, respectively. Furthermore, it was shown that the electrostatic potential from a particle follows a power law for large  $r$  (usually an  $r^{-6}$  decay) rather than the exponential decay of Debye screening. All this was shown by both statistical mechanical analysis and simulations. Thus, it is clear that one must include the dispersion interaction in the model potentials to obtain the correct qualitative behaviour of Coulomb fluids.

Note that the  $r^{-6}$  potential is introduced in the classical treatment as an effective potential that gives the leading term from quantum fluctuations not included in the classical theory. The presence of this interaction is not necessarily due to any internal electronic structure of the particles, it is also present for quantum point particles [1] due to the quantum fluctuations. In electrolytes the high-frequency contributions to the dispersion force are not screened by the ions since they move on a much slower time scale and cannot correlate with the high-frequency fluctuations.

In the current work we will primarily investigate a simple system, the one-component plasma (OCP), in order to more clearly bring out what distinguishes models for classical Coulomb fluids with and without dispersion-like interactions. We will thereby do an exact statistical mechanical analysis, including an explicit investigation of the bridge function. An interesting question is whether the exponential decay of the screening is simply replaced by a power law or whether an exponential component remains but is dominated by a power-law contribution for large  $r$ . We shall see that the latter is correct, but that the Coulombic  $r^{-1}$  and



**Figure 1.** A few bridge diagrams with  $h$ -bonds, density ( $n$ ) field points (black) and two root points (white) labelled 1 and 2. The first two diagrams have two cutting pairs of  $h$ -bonds each, the third has one and the last has none.

dispersion  $r^{-6}$  interactions have very intricate and interdependent effects on most aspects of the screening. This is much more clear in the OCP compared to many-component Coulombic systems, as we shall see.

We will make a full analysis of both cases with and without  $r^{-6}$  interactions in order to make the reasons for the different behaviours clear. We will limit the analysis to sufficiently small, but always finite densities in order to keep away from any critical points and other complications that may occur at higher concentrations.

## 2. Fluids with electrostatic and finite-ranged interactions

Let us consider a classical one-component plasma (OCP) with pair interaction potential

$$u(r) = u^{\text{Coul}}(r) + u^{\text{short}}(r) = \frac{q^2}{4\pi\epsilon_0 r} + u^{\text{short}}(r) \quad (1)$$

where  $r$  is the distance,  $u^{\text{Coul}}(r)$  is the Coulomb interaction,  $q$  is the particle charge,  $\epsilon_0$  is the permittivity of vacuum and  $u^{\text{short}}(r)$  is an arbitrary short-range potential that is zero outside a finite range, for example a hard core interaction (the results below will actually also be valid if  $u^{\text{short}}$  decays exponentially towards zero when  $r \rightarrow \infty$  with a decay length that is shorter than the decay length of the correlation functions). In addition, there is a neutralizing uniform charge density of opposite sign,  $-qn$ , that interacts with the particles, where  $n$  is the number density of the plasma.

The particle density distribution around a particle equals  $ng(r)$ , where  $g(r)$  is the pair distribution function, and the charge density  $\rho$  around a particle is  $\rho(r) = qnh(r)$ , where  $h(r) = g(r) - 1$ . The pair distribution function is given by

$$g(r) = \exp[-\beta u(r) + h(r) - c(r) + E(r)] \quad (2)$$

where  $\beta = (k_B T)^{-1}$ ,  $k_B$  is Boltzmann's constant,  $T$  is the absolute temperature,  $c(r)$  is the direct correlation function and  $E(r)$  is the bridge function. The functions  $h$  and  $c$  satisfy the Ornstein-Zernike (OZ) equation

$$h(r) = c(r) + \int d\mathbf{r}' c(|\mathbf{r} - \mathbf{r}'|) n h(r'). \quad (3)$$

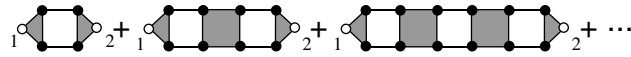
The bridge function is a functional of  $h$  and it can be written as an infinite series of bridge diagrams with  $h$  bonds and  $n$  field points [8] (a few such diagrams are shown in figure 1). These relationships determine  $h$  and  $c$  exactly and completely for a given  $u$  (the bridge functional constitute an exact closure).

The decay behaviour of  $h(r)$  for large  $r$  can be determined from the OZ equation provided the leading terms in the decay of  $c(r)$  are known. From equation (2) follows that the latter function is given by  $c(r) = -\beta u(r) + E(r) + h(r) - \ln[1 + h(r)]$  which implies that

$$c(r) + \beta u(r) \sim E(r) + \frac{1}{2} h^2(r) \quad \text{when } r \rightarrow \infty. \quad (4)$$

The decay behaviour of  $E(r)$  is in turn dominated by bridge diagrams with cutting pairs of  $h$ -bonds (the deletion of such a pair would cut all paths between the root points, cf figure 1) and we can write for large distances [9]

$$E(r_{12}) + \frac{1}{2}h^2(r_{12}) \sim e_2(r_{12}) = \quad (5)$$



where  $e_2(r_{12})$  is the sum of all diagrams with cutting pairs of  $h$ -bonds and the shaded faces in the diagrams are the sums of all appropriate subdiagrams that have no cutting pairs of bonds. These subdiagrams are hung together with cutting pairs of  $h$ -bonds as shown in the equation. The remaining diagrams of  $E$ , not contained in  $e_2$ , have only cutting triples, quadruplets, etc, of  $h$ -bonds like the last diagram in figure 1.

It is a rigorous result in classical statistical mechanics [1, 2] that in the limit of zero density we have

$$h(r) \sim A \exp(-\kappa r)/r \quad \text{when } r \rightarrow \infty, \quad (6)$$

where  $A$  and  $\kappa$  are the constants. In the zero density limit we have  $A \rightarrow q^2/(4\pi\epsilon_0)$  and  $\kappa \sim \kappa_D$ , where  $\kappa_D^2 = \beta n q^2/\epsilon_0$ , i.e. the result of the Debye–Hückel approximation is correct in this limit. The exponential decay behaviour in equation (6) holds as an exact result also for finite but sufficiently small densities [10, 11], but with different values of  $A$  and  $\kappa$  compared with the zero density limit and the Debye–Hückel approximation. We then have [11]  $A = (q^*)^2/(4\pi\epsilon^*)$  and  $\kappa^2 = \beta n q q^*/\epsilon_0$ , where  $q^* \neq q$  is an effective charge of the particles and  $\epsilon^* \neq \epsilon_0$  is an effective permittivity of the fluid. The short-ranged potential  $u^{\text{short}}$  affects the values of  $\kappa$ ,  $q^*$  and  $\epsilon^*$  but not the functional form of the decay. Let us investigate how these results are possible.

The leading terms in the asymptotic decay of a function for large  $r$  are, quite generally, associated with singularities of its Fourier transform. From an analysis of the latter, one can determine the former. Different kinds of functional dependence of the decay correspond to different kinds of singularities. (See [12] for a lucid description of the link between some kinds of singularities in  $k$ -space and the asymptotic decay in  $r$ -space as applied to fluids of electroneutral particles.) Thus, the asymptotic decay of  $h(r)$  is associated with singularities of its Fourier transform  $\hat{h}(k)$ ; the decay in equation (6) corresponds to simple poles at  $k = \pm i\kappa$  in complex  $k$ -space (by definition we take  $\pm i\kappa$  to denote the poles, if any, that lie closest to the real axis). It is sufficient to consider the upper half of complex  $k$ -space, so only the pole  $k = i\kappa$  needs to be considered (there will always be a corresponding pole at  $k = -i\kappa$  in the lower half space).

The OZ equation (3) implies that  $1 + n\hat{h}(k) = [1 - n\hat{c}(k)]^{-1}$  and hence poles are given by the solutions to  $n\hat{c}(k) = 1$ . Any other singularity of  $\hat{h}(k)$  is a consequence of that  $\hat{c}(k)$  too has a singularity, e.g. a branch point singularity. Not all singularities of  $\hat{c}(k)$  give rise to singularities of  $\hat{h}(k)$ . A pole of  $\hat{c}(k)$  is a regular point of  $\hat{h}(k)$ . Thus, to establish that the right-hand side (rhs) of equation (6) is indeed the leading term of  $h(r)$ , one can investigate the decay behaviour of  $c(r)$ . It is required that any singularity of  $\hat{c}(k)$  that is not a pole must be located further from the real axis in complex  $k$ -space than  $i\kappa$ . Then, the singularity gives rise to an asymptotic term in  $c(r)$  with a decay length shorter than  $1/\kappa$ . Note that the Coulomb potential has the Fourier transform  $\hat{u}^{\text{Coul}}(k) = q^2/(\epsilon_0 k^2)$ , so it contributes only with a pole.

The rigorous result (6) in the limit of zero density means that there is a pole of  $\hat{h}(k)$  which approaches  $i\kappa_D$  in this limit and that all other singularities go further away from the real axis than  $i\kappa_D$  or disappear when the density goes to zero. The pole will remain the leading singularity for finite, but possibly small, densities. To see how this is possible, we shall

perform two tasks: to establish the pole at  $i\kappa$  and to show that the leading asymptotic terms of  $c(r)$  for large  $r$  are such that they decay faster than  $h(r)$  (apart from terms corresponding to poles of  $\widehat{c}(k)$ ). More precisely we shall show that  $e_2(r) \sim O(h^2(r))$  for large  $r$  and hence  $c(r) + \beta u(r) \sim O(h^2(r))$ , cf equations (4) and (5). Note that these results imply that  $c(r) \sim -\beta u(r)$  for large  $r$ , a formula that is generally believed to be true.

Since  $u(r) \sim u^{\text{Coul}}(r)$  for large  $r$  it is useful to introduce the function  $c^0(r)$  from

$$c(r) = -\beta u^{\text{Coul}}(r) + c^0(r). \tag{7}$$

Equations (4) and (5) imply that  $c^0(r)$  decays like  $e_2(r)$  for large  $r$ . The OZ equation in Fourier space can be written as

$$1 + n\widehat{h}(k) = \frac{1}{1 - n\widehat{c}^0(k) + \kappa_D^2/k^2} = \frac{k^2/\kappa_D^2}{1 + [1 - n\widehat{c}^0(k)]k^2/\kappa_D^2} \tag{8}$$

where we have inserted  $n\beta\widehat{u}^{\text{Coul}}(k) = \kappa_D^2/k^2$ . The presence of the numerator,  $k^2/\kappa_D^2$ , and the fact that  $\widehat{c}^0(k)$  is finite for  $k = 0$  ensure that the local electroneutrality condition,  $q + \widehat{\rho}(0) = q[1 + n\widehat{h}(0)] = 0$ , and second moment condition are fulfilled.

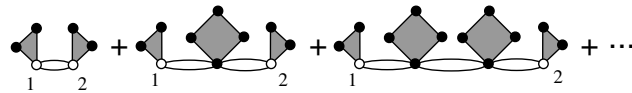
The denominator of equation (8) is zero for a pole of  $\widehat{h}(k)$ , in particular when  $k = i\kappa$ . This implies that  $\kappa$  satisfies

$$\kappa^2 = \kappa_D^2[1 - n\widehat{c}^0(i\kappa)]^{-1}, \tag{9}$$

which can be written as  $\kappa^2 = \beta n q q^*/\epsilon_0$ , where  $q^* = q[1 - n\widehat{c}^0(i\kappa)]^{-1}$ . One can show that  $n\widehat{c}^0(i\kappa) \rightarrow 0$  when  $n \rightarrow 0$  [11], so the pole exists at least for sufficiently low densities. Furthermore, it follows that  $q^* \rightarrow q$  and  $\kappa \sim \kappa_D$  in the zero density limit, i.e. the Debye–Hückel results are recovered in this limit. (In [11] a correlation function  $h^0(r)$  is introduced that satisfies  $1 + n\widehat{h}^0(k) = [1 - n\widehat{c}^0(k)]^{-1}$ . The function  $\rho^0(r)$ , defined from  $\widehat{\rho}^0(k) = q[1 + n\widehat{h}^0(k)]$ , constitutes the charge distribution of a dressed ion—a charge renormalization of the ion. The quantity  $q^* = \widehat{\rho}^0(i\kappa)$  is the effective point charge that represents the dressed ion charge.)

To investigate the decay behaviour of  $c(r)$ , cf equation (4), we will first consider the decay of  $E(r_{12}) + \frac{1}{2}h^2(r_{12})$  in equation (5). When  $h(r)$  decays exponentially like equation (6) the bridge diagrams with cutting pairs of  $h$ -bonds (i.e., those in  $e_2(r)$ ) behave asymptotically in the following manner [11] for large  $r$ :

$$E(r_{12}) + \frac{1}{2}h^2(r_{12}) \sim e_2(r_{12}) \sim \tag{10}$$



where each shaded face in the diagram now contributes as a number and the faces are linked by  $h^2$ -bonds. The first diagram decays like  $B_1 h^2(r_{12})$ , where  $B_1$  is a constant, i.e., proportionally to  $\exp(-2\kappa r)/r^2$ , and the other ones decay like convolutions of  $h^2$ . One can show that the second diagram decays like  $B_2 h^2(r_{12}) \ln(r_{12})$  and the following ones like  $B_\nu h^2(r_{12}) f_\nu(r_{12})$ , where  $B_\nu, \nu \geq 1$ , are constants and  $f_\nu(r_{12})$  are functions that are slowly varying for large  $r_{12}$ . When the expansion is summed to infinite order one obtains [11]  $e_2(r_{12}) \sim B_\infty h^2(r_{12}) f_\infty(r_{12})$ , where  $B_\infty$  is a constant,

$$f_\infty(x) = \int_0^\infty \frac{\zeta x \exp(-\zeta x t)}{\ln^2(t) + \pi^2} dt \tag{11}$$

and  $\zeta$  is another constant (all constants are state dependent). The Fourier transform of  $h^2(r_{12})$  has a logarithmic branch point singularity at  $k = i2\kappa$ , which correspond to the leading decay term that decays like  $\exp(-2\kappa r)/r^2$ . The Fourier transforms of all functions  $h^2(r_{12}) f_\nu(r_{12})$ ,

including  $\nu = \infty$ , also have branch point singularities at  $k = i2\kappa$  of various kinds and are analytic in the strip  $|\text{Im}(k)| < 2\kappa$  (we use the notation  $\text{Im}(\cdot)$  for the imaginary part and  $\text{Re}(\cdot)$  for the real part).

When extending the summation of the bridge diagrams to infinity, one has to make sure that no other singularity turns up that dominates the one at  $k = i2\kappa$ . All diagrams in equation (10) have branch point singularities in complex Fourier space at  $k = i2\kappa$ , but no singularities closer to the real axis. This implies that any *finite* sum of them will share the same property. One must make sure that the *infinite* sum of diagrams converges at least in the strip  $|\text{Im}(k)| < 2\kappa$ . For OCP, one can show that this indeed is the case, at least when the density is sufficiently low [11]. It is interesting to know that this is not always true. (For binary symmetric electrolytes, the restricted primitive model (RPM), the infinite sum diverges for  $k = i\tau$  with a positive  $\tau < 2\kappa$  [11]. This divergence makes the infinite sum to have a singularity (a simple pole) at  $k = i\tau$  and the dominating term in  $E_{ij}(r) + \frac{1}{2}h_{ij}^2(r)$  is a term  $T_{ij} e^{-\tau r}/r$  instead of the one proportional to  $h_{ij}^2(r)f_\infty(r)$ . One can show that when the electrolyte density goes to zero,  $\tau \rightarrow 2\kappa$  and  $T_{ij} \rightarrow 0$ , so this term becomes unimportant in the zero density limit.)

For large  $x$ , the function  $f_\infty(x)$  decays like  $1/\ln^2 x$  and hence from equation (4) we obtain

$$c(r) \sim -\beta u(r) + \frac{C e^{-2\kappa r}}{(r \ln r)^2} \quad \text{when } r \rightarrow \infty, \quad (12)$$

where  $C$  is a constant. This means that  $c^0(r)$  decays like the last term, which implies that  $\hat{c}^0(k)$  has a branch point singularity at  $k = i2\kappa$ . From equation (8) follows that  $\hat{h}(k)$  too has a branch point singularity there. This branch point gives rise to an asymptotic term in  $h(r)$  with a decay length  $1/(2\kappa)$ . Since it decays faster than the term shown in equation (6), the latter is the leading term as we anticipated above.

Finally, we shall investigate the electrostatic potential  $\psi(r)$  from a particle and the surrounding charge density  $\rho(r)$ . It can be obtained from the Poisson equation, which equals  $-\epsilon_0 k^2 \hat{\psi}(k) = q[1 + n\hat{h}(k)]$  in Fourier space. Thus, equation (8) implies that  $\hat{\psi}(k)$  also has a leading pole at  $k = i\kappa$  and hence it has the decay length  $1/\kappa$ . It decays like  $\psi(r) \sim q^* \exp(-\kappa r)/(4\pi\epsilon^* r)$  for large  $r$ , where  $\epsilon^* = \epsilon_0 + \beta q n [(2k)^{-1} d\hat{\rho}^0(k)/dk]_{k=i\kappa}$  [11].

To summarize, when the particles interact with a finite-ranged interaction apart from the Coulombic one, the pair distribution function and the electrostatic potential decay like  $\exp(-\kappa r)/r$  for large  $r$ , at least for sufficiently low density. The infinite summation of bridge diagrams brings in contributions that also decay exponentially, but with decay lengths that are shorter than  $1/\kappa$ . Analogous results hold for many-component electrolytes [11, 13] and will not be repeated here. As we shall see next, the dominance of exponential terms for large  $r$  is no longer true when the charged particles interact with  $r^{-6}$  potential in addition to those investigated here.

### 3. Fluids with electrostatic and dispersion-like interactions

#### 3.1. One-component plasma

Let us now consider classical Coulomb fluids with an  $r^{-6}$  contribution to the pair interaction potential. We first treat a one-component plasma (OCP) with pair potential

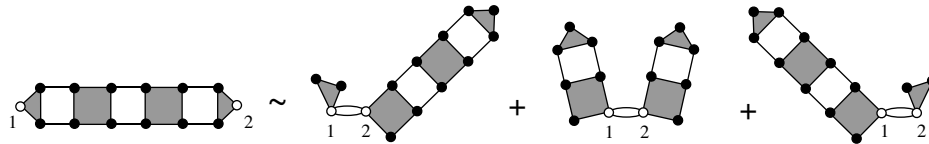
$$u(r) = u^{\text{Coul}}(r) + u^{\text{disp}}(r) + u^{\text{short}}(r) = \frac{q^2}{4\pi\epsilon_0 r} - \frac{\gamma}{r^6} + u^{\text{short}}(r), \quad (13)$$

where  $u^{\text{disp}}(r)$  gives the leading  $r^{-6}$  term in an effective dispersion interaction and  $\gamma$  is a positive constant (higher order power law terms can be added, but they will not change the

leading term in the decay of the distribution function). As before,  $u^{\text{short}}(r)$  is an arbitrary finite-ranged potential.

As we have seen above, the decay of  $h(r)$  can be determined via the OZ equation from the decay behaviour of  $c(r)$ . The latter is obtained from  $c(r) + \beta u(r)$ , which decays according to equation (4). We found that if  $h(r)$  decays exponentially then  $c(r) + \beta u(r)$  decays like  $h^2(r)$  times a slowly decaying function, equation (12), which implies that this contribution only gives rise to higher order terms in the decay of  $h(r)$ . The question is how the corresponding result looks like in the current case.

Stell [9] has shown that for a fluid of *electroneutral* particles interacting with a power law interaction  $-\lambda r^{-\nu}$  with  $\nu > 3$  as the leading term,  $h(r)$  has a power law decay and  $E(r) + \frac{1}{2}h^2(r)$  decays proportionally to  $h^2(r)$ . More precisely,  $h(r) \sim \beta K^2 \lambda r^{-\nu}$  for large  $r$ , where  $K = n\chi_T/\beta$  and  $\chi_T$  is the isothermal compressibility, and  $E(r) + \frac{1}{2}h^2(r)$  decays proportionally to  $r^{-2\nu}$  (this holds away from critical points). Thus,  $c(r) + \beta u(r)$  goes like  $h^2(r)$  in this case rather than  $h^2(r)$  times a slowly decaying function as in the previous one, but still this contribution only gives rise to higher order terms in the decay of  $h(r)$ . It is the power law decay of  $h(r)$  that changes the behaviour of the bridge diagrams compared to the situation with exponential decay. The result of Stell's analysis is that each term in  $e_2(r_{12})$ , equation (5), decays proportionally to  $h^2(r_{12})$  when  $h$  has a power law decay. For example, the last diagram displayed in equation (5) decays like



where the subdiagrams with field points in the rhs contribute as numbers and the root points are linked by an  $h^2$ -bond. The same applies to all other terms and the complete sum goes like a constant times  $h^2(r_{12})$ , where the constant consists of the contributions from the field point integrals (it is proportional to an integral of the third-order direct correlation function  $c^{(3)}$  and can be expressed as a thermodynamical quantity [9]). In general, we can conclude that  $c(r) + \beta u(r)$  decays much faster than  $h(r)$  (like  $O(h^2(r))$ ) when  $h(r)$  has either power law or exponential decay.

Let us return to our case with the pair potential (13). We have  $c(r) + \beta u(r) \sim e_2(r)$ , where  $e_2(r) \sim O(h^2(r))$  for large  $r$  provided that the decay of  $h(r)$  follows a power law or is exponential. If we define  $c^0(r)$  as above, equation (7), we have

$$c^0(r) \sim \frac{\beta\gamma}{r^6} + e_2(r) \quad \text{when } r \rightarrow \infty. \tag{14}$$

As before, the decay behaviour of a function for large  $r$  is linked to singularities of its Fourier transform. The presence of the  $r^{-6}$  contribution to  $c^0(r)$  implies that the small  $k$  power series expansion of  $\widehat{c}^0(k)$  has a term  $b|k|^3$  that is singular for  $k = 0$  at the real axis, where  $b = \pi^2\beta\gamma/12$ . (In complex  $k$ -space this term equals  $bk^3$  when  $\text{Re}(k) > 0$  and  $-bk^3$  when  $\text{Re}(k) < 0$ , with branch cuts along the imaginary axis. Henceforth, we shall only consider  $\text{Re}(k) \geq 0$  and write this term as  $bk^3$ .) Note that for a general function that decays faster than any power law for large  $r$  (sufficiently fast so all moments of the function are finite), its Fourier transform has a power series in  $k$  with only even powers in  $k$ . The appearance of an odd power in  $k$  corresponds to a function with power-law decay. In general, a term that decays for large  $r$  like an even-integer power law,  $ar^{-2m}$  with  $m \geq 2$ , implies that the Fourier transform has a term  $\alpha_m k^{2m-3}$  that is singular at  $k = 0$ , where  $\alpha_m = (-1)^{m+1} 2\pi^2 a / (2m - 2)!$ . (A function with an odd-integer power-law decay  $r^{-(2m+1)}$  with  $m \geq 2$  has instead a logarithmic kind of singularity at the origin, which case we need not be concerned with here.)



The Fourier transform of  $h(r)$  is given by equation (8). Our task is to determine the singularity of  $\widehat{h}(k)$  that gives rise to the leading term in the asymptotic decay of  $h(r)$  when  $r \rightarrow \infty$ . Let us first consider pole singularities. Any pole of  $\widehat{h}(k)$  satisfies  $[1 - n\widehat{c}^0(k)]k^2/\kappa_D^2 = -1$  and gives, as we have seen, rise to a term proportional to  $\exp(-\kappa r)/r$  where  $\kappa$  satisfies equation (9). This applies when the pole  $k = i\kappa$  lies on the imaginary axis, which was relevant above. It is also possible that poles lie off the imaginary axis and then the solution  $\kappa$  to equation (9) is a complex number (both  $\kappa$  and its complex conjugate are solutions in this case). This corresponds to an oscillatory, exponentially decaying term,  $h(r) \sim A \exp[-\text{Re}(\kappa)r] \cos(\text{Im}(\kappa)r + \varphi)/r$ , where  $A$  and  $\varphi$  are constants. The wavelength of the oscillation is  $2\pi|\text{Im}(\kappa)|^{-1}$  and the exponential decay length is  $\text{Re}(\kappa)^{-1}$ .

For the same reason as in section 2 above, the solution  $\kappa$  to equation (9) approaches  $\kappa_D$  in the zero density limit, so the leading pole lies off the real axis for finite densities (at least for small  $n$ ). Due to the occurrence of the term  $bk^3$  in  $\widehat{c}^0(k)$  there will, however, be a contribution  $inbk^3$  in the bracket of equation (9), which will prevent the existence of a solution with real  $\kappa$  when  $\gamma \neq 0$ , at least for small  $n$  (cf [12] where the corresponding phenomenon for electroneutral particles is treated). Thus, the contribution to  $h(r)$  from the leading pole  $i\kappa$  will be oscillatory and exponentially decaying. One can show from equation (9) that in the zero density limit we have  $\text{Im}(\kappa) \sim bn\kappa_D^4/2$  which is proportional to  $n^3$ , while  $\text{Re}(\kappa) \sim \kappa_D$  as usual which is proportional to  $n^{1/2}$ . This means that the wavelength will go to infinity faster than the decay length when the density decreases. At least for very low densities, the pole contribution to  $h(r)$  has therefore decayed to a very small value within a small fraction of the wavelength, so in practice there is very little difference between an oscillatory and non-oscillatory exponential decay. For higher densities, the oscillatory behaviour may, however, be significant in practice. (Do not confuse these oscillations with those that occur for OCP at high densities even in the absence of  $r^{-6}$  interactions. The mechanism for the occurrence of complex  $\kappa$  values and oscillations is entirely different here.)

In principle, it is very interesting that the presence of the dispersion interaction modifies the exponential term in the decay and makes it oscillatory. This term is, however, not the leading term in the decay of  $h(r)$ . Instead the leading term is a term with power law decay, as we now are going to see. Let us consider the small  $k$  expansion of  $1 + n\widehat{h}(k)$ . By expanding the rhs of equation (8) in a power series in  $[1 - n\widehat{c}^0(k)]k^2/\kappa_D^2$ , we obtain

$$1 + n\widehat{h}(k) = \frac{k^2}{\kappa_D^2} \left[ 1 - \frac{k^2}{\kappa_D^2}(1 - n\widehat{c}^0(k)) + \frac{k^4}{\kappa_D^4}(1 - n\widehat{c}^0(k))^2 + O(k^6) \right]. \quad (15)$$

One now inserts the small  $k$  expansion of  $\widehat{c}^0(k)$ , which contains singular contributions from the terms in equation (14). Note that  $\widehat{c}^0(k)$  is finite at  $k = 0$ . From equation (15) follows that the term  $bk^3$  in  $\widehat{c}^0(k)$  from  $u^{\text{disp}}$  gives rise to a contribution  $bk^7/\kappa_D^4$  in  $\widehat{h}(k)$ . Thus, there is a term  $r^{-10}$  in  $h(r)$ . This is the leading asymptotic contribution, so

$$h(r) \sim 1680 \frac{\Lambda}{r^{10}} \quad \text{when } r \rightarrow \infty, \quad (16)$$

where  $\Lambda = \beta\gamma/\kappa_D^4$  and  $1680 = 8!/4! = \alpha_3/\alpha_5$ . The reason for separating  $\Lambda$  and the numerical factor 1680 will be apparent in the next section. Note that the power law decay of  $h(r)$  agrees with the results for the quantum OCP, which also has an  $r^{-10}$  decay of the pair correlations [1]. (For completeness, we note that equation (16) implies that  $e_2(r)$  decays proportionally to  $r^{-20}$  and hence from equation (14) it follows that there is also a  $k^{17}$  term in  $\widehat{c}^0(k)$ , which gives rise to higher order terms only.)

It follows from equation (16) that the charge distribution  $\rho(r)$  around a particle decays for large  $r$  like

$$\rho(r) \sim 1680 \frac{nq\Lambda}{r^{10}} \quad (17)$$

and the electrostatic potential  $\psi(r)$  like

$$\psi(r) \sim -30 \frac{nq\Lambda}{\epsilon_0 r^8}. \quad (18)$$

Thus, the exponential decay of the electrostatic potential turns into a power law decay for large  $r$  when there is a dispersion interaction present in the pair interaction.

Note that the electrostatic potential tail has *opposite sign* compared to the particle charge and that the charge distribution in the tail has the same sign as the latter. This may appear surprising since the electrostatic interaction with the central particle is repulsive. Let us consider the particles that surround a particle placed at the origin. Without loss of generality we assume that  $q > 0$ . The tail behaviour in equations (16)-(18) has *nothing* to do with the particle distribution close to the central particle; the finite-ranged potential contribution  $u^{\text{short}}$ , which is arbitrary, does not affect it in any way. The behaviour is inherent in the tails. The dispersion attraction to the central particle increases the particle density for large  $r$  compared to the bulk density. In the absence of particle charges this would lead to an  $r^{-6}$  decay of the density, but the electrostatic interactions make the  $r$  dependence to be steeper,  $r^{-10}$ , and to have a coefficient that depends on the particle charges via  $\kappa_D^4$  in the denominator of  $\Lambda$ . Consider the situation for a certain  $r$  value in the tail. The positive charge density on the outside (for larger  $r$ ) must make the net charge on the inside to be negative due to electroneutrality. This implies an electrostatic interaction that enhances the attraction for a particle towards the centre. These effects conspire to make the density to decrease steeper and go like  $r^{-10}$ .

The appearance of  $\kappa_D^4$  in the denominator of  $\Lambda$  makes the coefficient in equation (16) to be larger when the density decreases. This is due to a decreased electrostatic screening.  $\Lambda$  is also increased when  $q$  is decreased or  $T$  is increased. The range of validity of the  $r^{-10}$  asymptotic term may, however, change at the same time, so one would have to go to larger and larger  $r$  values to remain in the asymptotic regime (i.e., where the  $r^{-10}$  decay is valid to a good approximation). This most likely happen when  $q$  is decreased while  $n$  is kept constant. Let us make a thought experiment where  $q$  is changed continuously. We know that when  $q = 0$  there is an asymptotic  $r^{-6}$  decay all the way to infinity, while for non-zero, albeit small,  $q$  there must always be an ultimate  $r^{-10}$  decay for very large  $r$ . This change between  $r^{-10}$  and  $r^{-6}$  decays ought to take place continuously when  $q \rightarrow 0$ . The  $r^{-10}$  decay will then occur only beyond some point that moves to a larger and larger  $r$  value when  $q \rightarrow 0$ . This decay is replaced below this point (i.e., for smaller  $r$ ) by an approximate  $r^{-6}$  decay, the range of which extends further and further out. This scenario is in agreement with the following observation for the middle term in equation (8):  $\kappa_D^2/k^2$  in the denominator has a non-negligible contribution compared to  $-nbk^3$  (from  $-n\hat{c}^0(k)$ ) only for smaller and smaller  $k$  values when  $\kappa_D \rightarrow 0$  and  $n$  is constant. It is the behaviour of the Fourier transform in the immediate neighbourhood of  $k = 0$  that determines the ultimate decay for very large  $r$  values.

To summarize, for the OCP in the absence of  $u^{\text{disp}}$  the functions  $h(r)$  and  $\psi(r)$  have  $\exp(-\kappa r)/r$  decays, but when  $u^{\text{disp}}$  is turned on these functions instead acquire leading  $r^{-10}$  and  $r^{-8}$  decays, respectively. There still remains an exponentially decaying contribution, but it becomes oscillatory in the presence of  $u^{\text{disp}}$ . If we instead start with electroneutral particles with  $u^{\text{disp}}$  interactions and turn on the Coulomb interactions, the initial  $r^{-6}$  decay of  $h(r)$  is changed to an  $r^{-10}$  decay. These features demonstrate that the Coulomb and dispersion interactions are coupled in an intricate manner in the classical OCP.

### 3.2. Comparison with many-component Coulomb fluids

Let us now compare the OCP with Coulomb fluids consisting of more than one ionic species, in particular binary electrolytes which have been investigated in [7]. In the latter case,  $h_{ij}(r)$  has an  $r^{-6}$  rather than  $r^{-10}$  decay in the presence of  $u_{ij}^{\text{disp}} = -\gamma_{ij}/r^6$ . In fact,  $h_{ij}(r) \sim \beta K^2 \gamma_{NN} r^{-6}$ , where  $\gamma_{NN}$  is a linear combination of  $\gamma_{ij}$  for the ionic species; a decay law that is like that for electroneutral particles mentioned above. This decay of  $h_{ij}(r)$  originates from the density–density correlations,  $h_{NN}(r)$ , in the binary Coulomb fluid. These correlations decay like  $h_{NN}(r) \sim \Lambda_{NN} r^{-6}$ , where  $\Lambda_{NN} = \beta K^2 \gamma_{NN}$ , while the charge–charge correlations,  $h_{QQ}(r)$ , have an  $r^{-10}$  decay exactly like in equation (16) with a coefficient  $1680\Lambda_{QQ}$ . The difference between OCP and multi-component electrolytes is due to the fact that density–density and charge–charge correlations are forced to be identical for the OCP while they are distinct in the other cases. It is the charges that ‘take control’ in the OCP as regards the asymptotics.

Let us specialize to a binary symmetric electrolyte (RPM with added dispersion term) with coefficients  $\gamma_{++} = \gamma_{--} \neq \gamma_{+-}$  for the two ionic species. For the RPM, we have  $h_{QQ} = (h_{++} - h_{+-})/2$  and  $h_{NN} = (h_{++} + h_{+-})/2$ , while the charge–density correlation function  $h_{QN}$  is identically zero. In this case the charge distribution around a particle decays exactly like equation (17) and the electrostatic potential exactly like equation (18), but with a coefficient  $\Lambda_{QQ} = \beta(\gamma_{++} - \gamma_{+-})/(2\kappa_D^4)$  instead of  $\Lambda$  [7]. The similarity to the OCP follows from the fact that  $h_{QQ}$  and  $c_{QQ}^0$  satisfy equation (8). An interesting special case occurs when  $\gamma_{++} = \gamma_{--} = \gamma_{+-}$ , so  $\Lambda_{QQ} = 0$ . Then,  $h_{QQ}(r)$  for the symmetric electrolyte decays *faster than any power law* (exponentially), while  $h_{NN}(r)$  has the same  $r^{-6}$  decay as before. In this case, the charge–charge and density–density correlations are asymptotically decoupled from each other to all orders. (It is well known that the OZ equations for  $h_{QQ}$  and  $h_{NN}$  are decoupled in this case; a decoupling to first-order terms. The decoupling to all orders follows from the fact that the bridge functions  $e_{QQ}$  and  $e_{NN}$  are also asymptotically decoupled [7].)

For a general binary electrolyte, we have  $h_{NN}(r) \sim \Lambda_{NN} r^{-6}$ ,  $h_{QN}(r) \sim -30\Lambda_{QN} r^{-8}$  and  $h_{QQ}(r) \sim 1680\Lambda_{QQ} r^{-10}$ , where the expression for  $\Lambda_{QQ}$  is more complicated than above [7]. These power laws are exactly the same as for quantum Coulomb fluids. Provided the  $u_{ij}^{\text{disp}}$  coefficients satisfy the ‘mixing rule’  $\gamma_{++}\gamma_{--} = \gamma_{+-}^2$  we have  $\Lambda_{NN}\Lambda_{QQ} = \Lambda_{QN}^2$ , also a mixing rule. (This motivates why the numerical factors are not included in the  $\Lambda$  coefficients. Also note that the application of the Laplace operator once to  $r^{-6}$  gives  $30r^{-8}$  and twice gives  $1680r^{-10}$ .)

The charge density around an ion of species  $j$  decays like  $\rho_j(r) \sim -30nq\Lambda_{QN}r^{-8}$  and the electrostatic potential like  $\psi_j(r) \sim nq\Lambda_{QN}\epsilon_0^{-1}r^{-6}$ , where  $q = (n_+q_+ + n_-|q_-|)/n$  and  $n = n_+ + n_-$ . Note that these power laws are different from the previous cases and that the sign of the tails here are the same for anions and cations.

We see that the OCP differs in detail from the multi-component case, but the general behaviour is the same with changes in the decay behaviour from exponential to power law decays when the dispersion term is switched on. An exponentially decaying contribution will remain in the electrostatic potential for the multi-component electrolyte when the dispersion is switched on, but it will become oscillatory for the same reason as for the OCP. The exponential term is dominated for large  $r$  by the power-law contributions. The complex interplay between the Coulomb and dispersion interactions is in many respects easier to track in the OCP due to its simplicity and because of the identity of the charge and density correlations in this case. We conclude that the dispersion interactions between the ions have profound effects on the screening behaviour of Coulomb fluids in general.

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