The one-component plasma: a conceptual approach

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Abstract

The one-component plasma (OCP) represents the simplest statistical mechanical model of a Coulomb system. For this reason, it has been extensively studied over the last 40 years. The advent of the integral equations has resulted in a dramatic improvement in our ability to carry out numerical calculations, but came at the expense of a physical insight gained in a simpler analytic theory. In this paper we present an extension of the Debye–Hückel (DH) theory to the OCP. The theory allows for analytic calculations of all the thermodynamic functions, as well as the structure factor. The theory explicitly satisfies the Stillinger–Lovett and, for small couplings, the compressibility sum rules, implying its internal self consistency. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

The classical one-component plasma (OCP) is an idealized system of N identical point-particles of charge q, in a uniform neutralizing background of dielectric constant D [1–3]. For concreteness we shall suppose that the particles are positively charged, while the background is negative. Each ion, inside the volume V, is assumed to interact with the others exclusively through the Coulomb potential. The OCP has been extensively studied because it serves as the simplest possible model for a variety of important physical systems, ranging from electrolytes and charge-stabilized colloids [4–7] to the dense stellar matter [8,9]. With the advent of powerful computers and new

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developments in the liquid-state theory our ability to perform thermodynamic calculations on this model has seen a dramatic improvement characterized, in particular, by the quantitative agreement between the integral-equations-based theories of the OCP and the Monte Carlo (MC) simulations [10,11]. Unfortunately, the intrinsic complexity of the integral equations, instead of clarifying the underlying physics, tends often to obscure it. This should be contrasted with the simplicity and the transparency of the Debye–Hückel (DH) theory [12,13], which allows for a very clear physical picture of an ionic solution.

Let us recall the early history of electrolyte solutions. The first modern ideas about electrolytes can be traced to the pionering work of the swedish physicist Svante Arrhenius [14] at the end of the last century. In particular, it was Arrhenius who realized that when salts and acids are dissolved in a polar solvent, the molecules become dissociated, producing cations and anions. Arguing from what can now be called mean-field point of view, Arrhenius concluded that, since the electrolyte solution is charge neutral and the ions are uniformly distributed, the average force acting on each particle is null. All the nontrivial characteristics of the electrolytes Arrhenius attributed to the incomplete dissociation of the molecules. In this simple picture an electrolyte is treated as an ideal gas composed of three species, cations, anions, and neutral molecules, whose densities are controlled by the law of mass action. All the electrostatic interactions are neglected *except* in as far as treating the cations and the anions as distinct entities. This simple theory has proven to work quite well for what are now known as weak electrolytes, such as Brønsted acids and bases. In the case of strong electrolytes, such as NaCl or HCl, the theory proved seriously flawed. It took almost 40 years before a satisfactory solution could be found. It appeared in the form of the now famous DH theory of strong electrolytes [12,13]. The great insight of Debye and Hückel was to realize that although the ions are *on average* uniformly distributed inside the solution, due to the long-range Coulomb force there exist strong correlations in the positions of the positively and the negatively charged particles; evidently in the vicinity of a positive ion there will be an excess of negative particles and vice versa.

To make this idea concrete and to see how it applies to the OCP, let us fix one mobile ion at the origin and ask what is the induced electrostatic potential in its surrounding. Clearly, this must satisfy the Poisson equation

$$\nabla^2 \phi(\mathbf{r}) = -\frac{4\pi}{D} \varrho(\mathbf{r}) \,. \tag{1}$$

To find the closure to this equation, we shall follow DH and suppose that the rest of the mobile ions arrange themselves in accordance with the Boltzmann distribution,

$$\varrho(\mathbf{r}) = q\bar{\rho}_+ \exp\left[-\beta q \phi(\mathbf{r})\right] - q\bar{\rho}_- \,, \tag{2}$$

where $\bar{\rho}_+ = N/V$ is the average density of the mobile ions, $\bar{\rho}_-$ is the density of the uniform neutralizing background, and $\beta = 1/k_B T$. The next step of the DH theory is to linearize the exponential factor, leading to

$$\varrho(\mathbf{r}) = -\frac{D\kappa_D^2}{4\pi} \phi(\mathbf{r}) \,, \tag{3}$$

where $\kappa_D = \sqrt{4\pi\lambda_B\bar{\rho}_+}$ and $\lambda_B = \beta q^2/D$ are the inverse Debye screening and the Bjerrum lengths, respectively. Clearly, the linearization can only be justified in the high-temperature (weak-coupling) limit. The resulting Helmholtz equation, $\nabla^2\phi(\mathbf{r}) = \kappa_D^2\phi(\mathbf{r})$, can be easily integrated to produce a potential of the Yukawa form. The fundamental lesson of DH is that the ions arrange themselves in such a way as to screen the long-range Coulomb interaction. It is this renormalization of the interaction potential that is responsible for the existence of the thermodynamic limit for Coulomb systems. However, not everything is rosy with this simple theory. It is sufficient to look at the charge–density distribution

$$\varrho(\mathbf{r}) = -\frac{q\kappa_D^2}{4\pi r}\,e^{-\kappa_D r}\,, \tag{4}$$

to notice that something went seriously wrong.

Clearly, the physical restriction that $\varrho(\mathbf{r}) \geqslant -q\bar{\rho}_-$ is strongly violated in the region near the fixed ion. The problem can be traced back to the linearization of the Boltzmann factor, which is unjustified at short distances, since there the electrostatic potential is not small even for high temperatures. Fortunately, not all is lost. A simple solution to overcome this difficulty was suggested by Nordholm [15,16], who proposed an augmentation of the DH theory to include an effective spherical cavity around the fixed ion, inside which no other ions can penetrate. The presence of such a cavity is quite reasonable, since the electrostatic repulsion between the like-charged ions should prevent them from coming into close contact. Furthermore, we can estimate the size of the hole, h, by comparing the repulsive Coulomb energy with the kinetic thermal energy, $q^2/Dh \sim k_B T$, or $h \sim q^2/Dk_B T$. Evidently, the higher the temperature, the smaller the size of the exclusion region. This, of course, is intuitive, since at higher temperatures the ions will have more kinetic energy to overcome the mutual repulsion. A more consistent way of defining the hole size h is to require an overall charge neutrality [15,16], or, equivalently, the continuity of the potential and of the electric field across the hole boundary. Performing a simple calculation, we find

$$h = d\left[\omega(\Gamma) - 1\right]/\sqrt{3\Gamma}\,, \tag{5}$$

$$\omega(\Gamma) = \left[1 + (3\Gamma)^{3/2}\right]^{1/3}\,, \tag{6}$$

where we have defined the usual coupling constant for the OCP, $\Gamma = \beta q^2/Dd$, and d is the characteristic length scale, $d = \left(4\pi\bar{\rho}_+^3/3\right)^{-1}$. In the low-coupling limit this reduces to the energetically determined expression for the size of the cavity, $h = \lambda_B$. Nordholm was able to demonstrate that this Debye–Hückel plus hole (DHH) theory produces an equation of state for the OCP which is in good agreement with the MC simulations. The question, however, still remains to what extent the hole is a physical object or just a convenient mathematical trick to correct for the linearization of the Poisson–Boltzmann (PB) equation. Clearly, if the cavity postulated by the DHH theory is real, the best way to study it is by considering the structure factor. In particular, if everything is all right with the DHH theory, the structure factor obtained on its basis

should be in good agreement with the MC simulations. Unfortunately, it is well known that the traditional ways of obtaining the correlation functions out of the DH theory lead to expressions which are seriously flawed [17,18]. In the case of the restricted primitive model (RPM), the correlation functions violate the well-known Stillinger–Lovett sum rules [19,20] and do not reproduce the charge–density oscillations known to exist at high densities [21].

Recently, Lee and Fisher [17,18] have proposed an extension of the DH theory of strong electrolytes to nonuniform densities. The generalized DH theory (GDH) allows the calculation of the density–density and of the charge–charge correlation functions in a most natural way, through a functional differentiation of the free-energy functional. Furthermore, since the theory is constructed at the level of free energy, it is internally self-consistent, as can be judged by the various sum rules that it satisfies. This, of course, is a great advantage over the traditional integral-equations-based theories, which are constructed at the level of the correlation functions and depend on the route taken to thermodynamics [1], i.e. virial, compressibility, etc. The comparison of the GDH theory with experiments or simulations, however, is made difficult by the same flaw (or virtue, depending on how one looks at it) that the original DH theory suffers, its linearity. The linearity of the DH theory for electrolytes is both a blessing and a curse. It ensures the internal self-consistency of the theory, but is also responsible for undercounting the configurations in which the oppositely charged ions come into a close contact, forming dipolar pairs. It was shown recently how this difficulty can be overcome in the context of the Debye–Hückel–Bjerrum (DHBj) theory [24–26], by allowing for the existence of a chemical equilibrium between the monopoles and dipoles. Unfortunately, this stratagem is difficult to implement in the case of the GDH theory. The goal of this paper, then, is twofold: test the physical nature of the cavity in the DHH theory and, by apply the GDH theory to the OCP – which is free from the cluster formations that plague RPM – test the extent of its validity.

2. The generalized Debye–Hückel theory for the one-component plasma

The DHH theory for the OCP is extended to allow for a nonuniform, slowly varying ionic density,

$$\rho_+(\boldsymbol{r}) = \bar{\rho}_+ \left(1 + \Delta \cos \boldsymbol{k} \cdot \boldsymbol{r}\right) . \tag{7}$$

The negative background, as in the original OCP theory, is maintained uniform,

$$\rho_-(\boldsymbol{r}) = \bar{\rho}_-, \quad \forall \boldsymbol{r} . \tag{8}$$

To preserve the electroneutrality on long-length scales, the overall equilibrium densities must be equal, $\bar{\rho}_+ = \bar{\rho}_-$.

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[1] One should mention, however, integral equations such as the generalized mean-spherical approximation (GMSA), Ref. [22] and the self-consistent Ornstein-Zernike approximation (SCOZA), Ref. [23], which were constructed to explicitly enforce the self-consistency.

The Helmholtz free-energy, F, is a functional of the ionic density $\rho_+(r)$. The direct correlation function, $C_{++}(r_1 - r_2)$, is defined in terms of the second derivative of the excess free energy,

$$C_{++}(r_1 - r_2) \equiv -\beta \left. \frac{\delta^2 \{F[\rho_+(r)] - F_{\text{ideal}}[\rho_+(r)]\}}{\delta\rho_+(r_1)\,\delta\rho_+(r_2)} \right|_{\rho_+(r) = \bar{\rho}_+}$$

$$= \frac{\delta(r_1 - r_2)}{\bar{\rho}_+} - \beta \left. \frac{\delta^2 F[\rho_+(r)]}{\delta\rho_+(r_1)\,\delta\rho_+(r_2)} \right|_{\rho_+(r) = \bar{\rho}_+} . \tag{9}$$

Here, $F_{\text{ideal}}[\rho_+(r)]$ is the usual ideal-gas Helmholtz free-energy functional,

$$\beta F_{\text{ideal}}[\rho_+(r)] = \int d^3r'\, \rho_+(r') \left\{ \ln\left[\rho_+(r')\Lambda^3\right] - 1 \right\} , \tag{10}$$

where Λ is the thermal de Broglie wavelength.

The direct correlation function is connected with the total correlation function, $H(r)$, through the Ornstein–Zernike relation,

$$H(r) = C_{++}(r) + \bar{\rho}_+ \int d^3r'\, C_{++}(r - r')H(r') , \tag{11}$$

which in the Fourier space can be written as

$$\hat{H}(k) = \frac{\hat{C}_{++}(k)}{1 - \bar{\rho}_+ \hat{C}_{++}(k)} , \tag{12}$$

where $\hat{C}_{++}(k)$ and $\hat{H}(k)$ are the Fourier transforms of the direct and the total correlation functions, respectively,

$$\hat{C}_{++}(k) = \int d^3r\, C_{++}(r)\exp(ik \cdot r) , \tag{13}$$

$$\hat{H}(k) = \int d^3r\, H(r)\exp(ik \cdot r) . \tag{14}$$

The structure factor is defined as

$$S(k) \equiv 1 + \bar{\rho}_+ \hat{H}(k) = \frac{1}{1 - \bar{\rho}_+ \hat{C}_{++}(k)} . \tag{15}$$

Evidently, the knowledge of the direct correlation function $C_{++}(r)$ is equivalent to the knowledge of the structure factor $S(k)$.

To proceed, we impose an infinitesimal variation on the mobile-ion density, Eq. (7), and expand the reduced Helmholtz free-energy functional density, $f \equiv \beta F/V$, in powers of Δ. To second order, the variation δf can be written as (see details in Appendix B)

$$\delta f[\rho_+(r)] \equiv f[\rho_+(r)] - f[\bar{\rho}_+] = \beta\bar{\mu}\bar{\rho}_+ \Delta\delta_{k0} + \tfrac{1}{4}S^{-1}(k)\bar{\rho}_+\Delta^2(1 + \delta_{k0}) , \tag{16}$$

where $\beta\bar{\mu} = \partial f/\partial\bar{\rho}_+$ is the equilibrium chemical potential, $\delta_{k0} = 1/V(2\pi)^3\delta^3(k)$ is the Kronecker delta and $\delta^3(k)$ is the three-dimensional Dirac delta function. The

free-energy density of the homogeneous reference system, $f[\bar\rho_+]$, is obtained by setting $\varDelta = 0$ in the expression for $f[\rho_+(r)]$. Clearly, if we are able to construct the free-energy functional for a nonuniform system, the structure factor, $S(\boldsymbol{k})$, can be read directly from the second-order term.

We proceed in a way exactly analogous to the usual DH theory. Let us fix one positive ion at $\boldsymbol{r}'$ and ask what is the electrostatic potential, $\phi(\boldsymbol{r},\boldsymbol{r}')$, at a point $\boldsymbol{r}$ in its surrounding. We shall assume that, just like in the uniform case, this potential satisfies the PB equation,

$$\nabla_r^2 \phi(\boldsymbol{r},\boldsymbol{r}') = -\frac{4\pi q}{D}\left\{\delta^3(\boldsymbol{r}-\boldsymbol{r}') + \rho_+(\boldsymbol{r})\exp\left[-\beta q \tilde\phi(\boldsymbol{r},\boldsymbol{r}')\right] - \rho_-(\boldsymbol{r})\right\}. \tag{17}$$

A crucial point to remark [17,18] is that the potential which appears in the Boltzmann factor of (17), $\tilde\phi(\boldsymbol{r},\boldsymbol{r}')$, represents a *local-induced* potential,

$$\tilde\phi(\boldsymbol{r},\boldsymbol{r}') \equiv \phi(\boldsymbol{r},\boldsymbol{r}') - \varPhi(\boldsymbol{r}), \tag{18}$$

obtained by extracting from the total potential $\phi(\boldsymbol{r},\boldsymbol{r}')$ an *imposed* electrostatic potential, $\varPhi(\boldsymbol{r})$, produced by the neutralizing background and the imposed charge–density variation (7),

$$\nabla^2 \varPhi(\boldsymbol{r}) = -\frac{4\pi q}{D}\left[\rho_+(\boldsymbol{r}) - \bar\rho_-\right] = -\frac{4\pi q \bar\rho_+}{D}\varDelta\cos\boldsymbol{k}\cdot\boldsymbol{r}, \qquad \forall\boldsymbol{r}. \tag{19}$$

With the separation of the total potential $\phi(\boldsymbol{r},\boldsymbol{r}')$ into two parts, the Helmholtz free-energy functional can be written as

$$F[\rho_+(\boldsymbol{r})] = F_{\text{ideal}}[\rho_+(\boldsymbol{r})] + F_{\text{imposed}}[\rho_+(\boldsymbol{r})] + F_{\text{induced}}[\rho_+(\boldsymbol{r})], \tag{20}$$

where the excess free energies are obtained through the Debye charging process [12,13, 17,18],

$$F_{\text{imposed}}[\rho_+(\boldsymbol{r})] = q\int d^3\boldsymbol{r}'\left[\rho_+(\boldsymbol{r}') - \bar\rho_-\right]\int_0^1 d\lambda\,\varPhi(\boldsymbol{r}',\lambda q), \tag{21}$$

$$F_{\text{induced}}[\rho_+(\boldsymbol{r})] = q\int d^3\boldsymbol{r}'\,\rho_+(\boldsymbol{r}')\int_0^1 d\lambda\,\psi(\boldsymbol{r}',\lambda q). \tag{22}$$

In Eq. (22), $\psi(\boldsymbol{r}')$ is the *mean-induced* electrostatic potential felt by the positive ion fixed at $\boldsymbol{r}'$,

$$\psi(\boldsymbol{r}') \equiv \lim_{\boldsymbol{r}\to\boldsymbol{r}'}\left[\tilde\phi(\boldsymbol{r},\boldsymbol{r}') - \frac{q}{D|\boldsymbol{r}-\boldsymbol{r}'|}\right]. \tag{23}$$

Linearization of the Boltzmann factor of (17) results in the GDH equation for the induced potential,

$$\nabla_r^2 \tilde\phi(\boldsymbol{r},\boldsymbol{r}') = -\frac{4\pi q}{D}\left[\delta^3(\boldsymbol{r}-\boldsymbol{r}') - \rho_+(\boldsymbol{r})\right]$$

$$= -\frac{4\pi q}{D}\left[\delta^3(\boldsymbol{r}-\boldsymbol{r}') - \bar\rho_+(1 + \varDelta\cos\boldsymbol{k}\cdot\boldsymbol{r})\right] \quad \text{for } |\boldsymbol{r}-\boldsymbol{r}'| \leqslant h, \tag{24}$$

$$\nabla_r^2 \tilde{\phi}(r,r') = \frac{4\pi\beta q^2 \rho_+(r)}{D}\, \tilde{\phi}(r,r')$$

$$= \kappa_D^2 \left(1 + \Delta \cos k \cdot r\right) \tilde{\phi}(r,r') \quad \text{for } |r - r'| \geqslant h \,. \tag{25}$$

As discussed in the introduction, to prevent the unphysical artifacts of linearization of the PB equation, we have explicitly introduced a cavity of radius h around the fixed ion at r', given by Eq. (5), into which no other mobile ions can penetrate.

In the following subsections we shall obtain the contributions to the variation of the free-energy density.

2.1. The ideal-gas contribution

The ideal-gas contribution is given by (10) with the imposed mobile-ion charge distribution (7). Expanding (10) up to order Δ^2 and using integrals (A.3) and (A.4), we obtain the ideal-gas contribution to the variation of the reduced free-energy density,

$$\delta f_{\text{ideal}}\left[\rho_+(r)\right] = \ln\left(\bar{\rho}_+ \Lambda^3\right) \bar{\rho}_+ \Delta \delta_{k0} + \tfrac{1}{4}\bar{\rho}_+ \Delta^2 \left(1 + \delta_{k0}\right) \,. \tag{26}$$

2.2. The imposed electrostatic potential contribution

The imposed electrostatic potential satisfies the Poisson equation (19), whose formal solution can be written as

$$\Phi(r) = \frac{q\bar{\rho}_+}{D}\Delta \int d^3r' \, \frac{\cos k \cdot r'}{|r - r'|} \,. \tag{27}$$

The contribution to the Helmholtz free-energy functional is obtained through the Debye charging process [12,13],

$$F_{\text{imposed}}\left[\rho_+(r)\right] = q \int d^3r' \left[\rho_+(r') - \bar{\rho}_-\right] \int_0^1 d\lambda \, \Phi(r', \lambda q)$$

$$= \frac{q^2 \bar{\rho}_+^2}{D}\Delta^2 \int d^3r\, d^3r' \, \frac{\cos k \cdot r \cos k \cdot r'}{|r - r'|} \int_0^1 d\lambda \, \lambda \,. \tag{28}$$

In this case the charging merely produces a trivial factor of 1/2 and using integral (A.7), we obtain the contribution of the imposed electrostatic potential to the variation of the reduced free-energy density,

$$\delta f_{\text{imposed}}\left[\rho_+(r)\right] = \frac{1}{4}\left(\frac{\kappa_D}{k}\right)^2 \bar{\rho}_+ \Delta^2 \left(1 + \delta_{k0}\right) \,. \tag{29}$$

2.3. The induced electrostatic potential contribution

The induced electrostatic potential satisfies the GDH equation, given by (24) and (25). It is convenient to rewrite them in a spherical coordinate system centered on the positive ion fixed at r'. Introducing the difference vector

$$R = r - r' \,, \tag{30}$$

the GDH equation for the induced electrostatic potential reads

$$\nabla_R^2 \tilde{\phi}(\boldsymbol{R} + \boldsymbol{r}', \boldsymbol{r}') = \begin{cases} -\dfrac{4\pi q}{D}\left\{\delta^3(\boldsymbol{R}) - \bar{\rho}_+\left[1 + \Delta\cos\boldsymbol{k}\cdot(\boldsymbol{R}+\boldsymbol{r}')\right]\right\} & \text{for } |\boldsymbol{R}| \leqslant h, \\ \kappa_D^2\left[1 + \Delta\cos\boldsymbol{k}\cdot(\boldsymbol{R}+\boldsymbol{r}')\right]\tilde{\phi}(\boldsymbol{R}+\boldsymbol{r}',\boldsymbol{r}') & \text{for } |\boldsymbol{R}| \geqslant h. \end{cases} \tag{31}$$

Using the Green's function, $G(\boldsymbol{R}, \boldsymbol{R}')$, associated with (31) derived in appendix C, it can be transformed into an integral equation

$$\tilde{\phi}(\boldsymbol{r}, \boldsymbol{r}') = \tilde{\phi}(\boldsymbol{R} + \boldsymbol{r}', \boldsymbol{r}') = \frac{1}{D}\int d^3\boldsymbol{R}'\, \varrho(\boldsymbol{R}')\, G(\boldsymbol{R}, \boldsymbol{R}')\,, \tag{32}$$

where the effective charge density, $\varrho(\boldsymbol{R})$, is given by

$$\varrho(\boldsymbol{R}) = \begin{cases} q\delta^3(\boldsymbol{R}) - q\bar{\rho}_+\left[1 + \Delta\cos\boldsymbol{k}\cdot(\boldsymbol{R}+\boldsymbol{r}')\right] & \text{for } R \leqslant h, \\ -\dfrac{D}{4\pi}\kappa_D^2\tilde{\phi}(\boldsymbol{R}+\boldsymbol{r}',\boldsymbol{r}')\,\Delta\cos\boldsymbol{k}\cdot(\boldsymbol{R}+\boldsymbol{r}') & \text{for } R \geqslant h. \end{cases} \tag{33}$$

This equation can be solved perturbatively in powers of Δ (see Appendix D).

The mean induced electrostatic potential felt by the positive ion fixed at $\boldsymbol{r}'$,

$$\psi(\boldsymbol{r}') = \lim_{\boldsymbol{R}\to 0}\left[\tilde{\phi}(\boldsymbol{R}+\boldsymbol{r}',\boldsymbol{r}') - \frac{q}{DR}\right]\,, \tag{34}$$

can be written, to order Δ^2, as (see derivation in Appendix D)

$$\begin{aligned}
\beta q\psi(\boldsymbol{r}') = &-\frac{1}{2}x(x+2) - \Delta\cos\boldsymbol{k}\cdot\boldsymbol{r}'\left[\frac{1}{\alpha^2} - \frac{\sin\alpha x}{\alpha^3(1+x)} - \frac{\cos\alpha x}{\alpha^2(1+x)} + \frac{x}{1+x}\mathscr{I}_0^+(x,\alpha)\right] \\
&+ \frac{1}{\alpha(1+x)}\Delta^2\sum_{\ell=0}^{\infty}(2\ell+1)\cos^2\left(\boldsymbol{k}\cdot\boldsymbol{r}' + \ell\frac{\pi}{2}\right)\frac{x^{\ell+2}j_{\ell+1}(\alpha x)}{g_{\ell+1}(x)}\mathscr{I}_\ell^+(x,\alpha) \\
&+ \frac{x}{1+x}\Delta^2\sum_{\ell=0}^{\infty}(-1)^{\ell+1}(2\ell+1)\cos^2\left(\boldsymbol{k}\cdot\boldsymbol{r}' + \ell\frac{\pi}{2}\right) \\
&\times\left\{\frac{1}{2}\frac{g_{\ell+1}(-x)}{g_{\ell+1}(x)}\left[\mathscr{I}_\ell^+(x,\alpha)\right]^2 + \mathscr{I}_\ell^+(x,\alpha)\mathscr{I}_\ell^-(x,\alpha) - \mathscr{I}_\ell^0(x,\alpha)\right\},
\end{aligned} \tag{35}$$

where $x = \kappa_D h$, $\alpha = k/\kappa_D$, $j_\ell(\xi)$ is the spherical Bessel function of the first kind,

$$j_\ell(\xi) = \sqrt{\frac{\pi}{2\xi}}\, J_{\ell+1/2}(\xi)\,, \tag{36}$$

$g_\ell(\xi)$ is the ℓth grade polynomial associated with the modified spherical Bessel function of the third kind, $k_\ell(\xi)$,

$$g_\ell(\xi) \equiv e^\xi \xi^{\ell+1} k_\ell(\xi) = \sum_{m=0}^{\ell}\frac{\Gamma(\ell+m+1)}{2^m m!\,\Gamma(\ell-m+1)}\xi^{\ell-m} = \sum_{m=0}^{\ell}\frac{(2m)!}{2^m m!}\binom{\ell+m}{2m}\xi^{\ell-m} \tag{37}$$

and $\{\mathscr{I}_\ell^\nu\}$, $\nu = \pm, 0$, are the one-dimensional quadratures

$$\mathscr{I}_\ell^-(s,\alpha) = \int_0^s d\xi\,\xi^{-\ell}g_\ell(-\xi)j_\ell(\alpha\xi)\,, \tag{38}$$

$$\mathscr{I}_\ell^0(x,\alpha) = \int_x^\infty \mathrm{d}s\, s^{-\ell} g_\ell(s) j_\ell(\alpha s) \mathscr{I}_\ell^-(s,\alpha) \exp\left[2(x-s)\right] , \tag{39}$$

$$\mathscr{I}_\ell^+(x,\alpha) = \int_x^\infty \mathrm{d}s\, s^{-\ell} g_\ell(s) j_\ell(\alpha s) \exp\left[2(x-s)\right] . \tag{40}$$

The contribution to the Helmholtz free-energy functional is obtained through the Debye charging process [12,13,17,18],

$$\begin{aligned}
F_{\text{induced}}\left[\rho_+(\boldsymbol{r})\right] &= q \int \mathrm{d}^3\boldsymbol{r}'\, \rho_+(\boldsymbol{r}') \int_0^1 \mathrm{d}\lambda\, \psi(\boldsymbol{r}',\lambda q) \\
&= q\bar\rho_+ \int \mathrm{d}^3\boldsymbol{r}'\, \left(1 + \Delta\cos\boldsymbol{k}\cdot\boldsymbol{r}'\right) \int_0^1 \mathrm{d}\lambda\, \psi(\boldsymbol{r}',\lambda q) ,
\end{aligned} \tag{41}$$

which yields the reduced free-energy density,

$$\begin{aligned}
f_{\text{induced}}\left[\rho_+(\boldsymbol{r})\right] &= \bar\rho_+ f_0 + \left[f_0 + \tfrac{1}{2}f_1(\alpha)\right]\bar\rho_+ \Delta\delta_{\boldsymbol{k}0} + \tfrac{1}{4}\left[f_1(\alpha)\right.\\
&\quad \left.+ f_2(\alpha)\right]\bar\rho_+ \Delta^2\left(1 + \delta_{\boldsymbol{k}0}\right) ,
\end{aligned} \tag{42}$$

from which the variation follows,

$$\begin{aligned}
\delta f_{\text{induced}}\left[\rho_+(\boldsymbol{r})\right] &= f_{\text{induced}}\left[\rho_+(\boldsymbol{r})\right] - f_{\text{induced}}\left[\bar\rho_+\right] \\
&= \left[f_0 + \tfrac{1}{2}f_1(\alpha)\right]\bar\rho_+ \Delta\delta_{\boldsymbol{k}0} + \tfrac{1}{4}\left[f_1(\alpha) + f_2(\alpha)\right]\bar\rho_+ \Delta^2\left(1 + \delta_{\boldsymbol{k}0}\right) ,
\end{aligned} \tag{43}$$

where

$$\begin{aligned}
f_0 &= -\frac{1}{2}\int_0^1 \frac{\mathrm{d}\lambda}{\lambda} x_\lambda(x_\lambda + 2) = -\frac{1}{2}\int_1^\omega \mathrm{d}\omega_\lambda\, \frac{\omega_\lambda^2(\omega_\lambda + 1)}{\omega_\lambda^2 + \omega_\lambda + 1} \\
&= \frac{1}{4}\left[1 - \omega^2 + \frac{2\pi}{3\sqrt{3}} + \ln\left(\frac{\omega^2 + \omega + 1}{3}\right) - \frac{2}{\sqrt{3}}\tan^{-1}\left(\frac{2\omega + 1}{\sqrt{3}}\right)\right] ,
\end{aligned} \tag{44}$$

$$\begin{aligned}
f_1(\alpha) &= -\frac{1}{\alpha^2} + \frac{2}{\alpha^3}\int_0^1 \mathrm{d}\lambda\, \frac{\lambda^2}{\omega_\lambda}\sin(\alpha x_\lambda/\lambda) + \frac{2}{\alpha^2}\int_0^1 \mathrm{d}\lambda\, \frac{\lambda}{\omega_\lambda}\cos(\alpha x_\lambda/\lambda) \\
&\quad -2\int_0^1 \frac{\mathrm{d}\lambda}{\lambda}\frac{\omega_\lambda - 1}{\omega_\lambda}\mathscr{I}_0^+(x_\lambda,\alpha/\lambda) ,
\end{aligned} \tag{45}$$

$$\begin{aligned}
f_2(\alpha) &= \sum_{\ell=0}^\infty (2\ell+1)\left[\frac{1+(-1)^\ell\delta_{\boldsymbol{k}0}}{1+\delta_{\boldsymbol{k}0}}\right]\left\{\frac{2}{\alpha}\int_0^1 \mathrm{d}\lambda\, \frac{x_\lambda^{\ell+2}j_{\ell+1}(\alpha x_\lambda/\lambda)}{\omega_\lambda\, g_{\ell+1}(x_\lambda)}\mathscr{I}_\ell^+(x_\lambda,\alpha/\lambda)\right.\\
&\quad + (-1)^{\ell+1}\int_0^1 \frac{\mathrm{d}\lambda}{\lambda}\frac{\omega_\lambda - 1}{\omega_\lambda}\left[\frac{g_{\ell+1}(-x_\lambda)}{g_{\ell+1}(x_\lambda)}\left[\mathscr{I}_\ell^+(x_\lambda,\alpha/\lambda)\right]^2\right.\\
&\quad \left.\left. +2\mathscr{I}_\ell^+(x_\lambda,\alpha/\lambda)\mathscr{I}_\ell^-(x_\lambda,\alpha/\lambda) - 2\mathscr{I}_\ell^0(x_\lambda,\alpha/\lambda)\right]\right\} ,
\end{aligned} \tag{46}$$

$$x_\lambda = \omega_\lambda - 1 , \tag{47}$$

$$\omega_\lambda = \left[1 + \lambda^3 \left(3\Gamma\right)^{3/2}\right]^{1/3}, \tag{48}$$

$$\omega = \omega_{\lambda=1} = \left[1 + \left(3\Gamma\right)^{3/2}\right]^{1/3}. \tag{49}$$

We note that the reduced induced free-energy density for the reference system,

$$f_{\text{induced}}\left[\bar{\rho}_+\right] = \bar{\rho}_+ f_0$$

$$= \frac{1}{4}\bar{\rho}_+\left[1 - \omega^2 + \frac{2\pi}{3\sqrt{3}} + \ln\left(\frac{\omega^2 + \omega + 1}{3}\right) - \frac{2}{\sqrt{3}}\tan^{-1}\left(\frac{2\omega + 1}{\sqrt{3}}\right)\right] \tag{50}$$

is the same as the one previously obtained by Nordholm [15,16].

3. Analytical results and the sum rules

Collecting all the contributions to the variation of the reduced free-energy density,

$$\delta f\left[\rho_+(\mathbf{r})\right] = \delta f_{\text{ideal}}\left[\rho_+(\mathbf{r})\right] + \delta f_{\text{imposed}}\left[\rho_+(\mathbf{r})\right] + \delta f_{\text{induced}}\left[\rho_+(\mathbf{r})\right] \tag{51}$$

and comparing with the expansion given by (16), we obtain the equilibrium chemical potential,

$$\beta\bar{\mu} = \ln\left(\bar{\rho}_+ \Lambda^3\right) + f_0 + \tfrac{1}{2}\lim_{\alpha\to 0} f_1(\alpha)$$

$$= \ln\left(\bar{\rho}_+ \Lambda^3\right) + f_0 + \tfrac{1}{12}\left(1 - \omega^2\right), \tag{52}$$

which corresponds to the usual OCP chemical potential [15,16], and the structure factor,

$$S^{-1}(\mathbf{k}) = 1 + \frac{2}{\alpha^3}\int_0^1 d\lambda\,\frac{\lambda^2}{\omega_\lambda}\sin(\alpha x_\lambda/\lambda) + \frac{2}{\alpha^2}\int_0^1 d\lambda\,\frac{\lambda}{\omega_\lambda}\cos(\alpha x_\lambda/\lambda)$$

$$- 2\int_0^1 \frac{d\lambda}{\lambda}\,\frac{\omega_\lambda - 1}{\omega_\lambda}\,\mathscr{I}_0^+(x_\lambda, \alpha/\lambda)$$

$$+ \sum_{\ell=0}^{\infty}(2\ell + 1)\left\{\frac{2}{\alpha}\int_0^1 d\lambda\,\frac{x_\lambda^{\ell+2}j_{\ell+1}(\alpha x_\lambda/\lambda)}{\omega_\lambda\,g_{\ell+1}(x_\lambda)}\,\mathscr{I}_\ell^+(x_\lambda, \alpha/\lambda)\right.$$

$$+ (-1)^{\ell+1}\int_0^1 \frac{d\lambda}{\lambda}\,\frac{\omega_\lambda - 1}{\omega_\lambda}\left[\frac{g_{\ell+1}(-x_\lambda)}{g_{\ell+1}(x_\lambda)}\left[\mathscr{I}_\ell^+(x_\lambda, \alpha/\lambda)\right]^2\right.$$

$$\left.+ 2\mathscr{I}_\ell^+(x_\lambda, \alpha/\lambda)\mathscr{I}_\ell^-(x_\lambda, \alpha/\lambda) - 2\mathscr{I}_\ell^0(x_\lambda, \alpha/\lambda)\right]\right\}. \tag{53}$$

This is the central result of this paper, the explicit expression for the structure factor of the OCP, given in terms of an infinite series. To check the internal consistency of the theory, we explore how well it satisfies various known sum rules. All these can be conveniently summarized in the exact, small $\mathbf{k}$ expansion of the structure factor [3],

$$S_{\text{exact}}^{-1}(\mathbf{k}) = \left(\frac{\kappa_D}{k}\right)^2 + \frac{\beta}{\bar{\rho}_+ \chi} + \mathcal{O}(k^2), \tag{54}$$

where χ is the compressibility of the OCP. The first term is the result of the charge neutrality and of the Stillinger–Lovett second-moment condition [19,20], while the second term corresponds to the fourth-moment or the "compressibility" sum rule [3]. The inverse compressibility is defined thermodynamically in terms of the variation of the pressure,

$$P = \frac{\bar{\rho}_+}{\beta}\left(1 + \bar{\rho}_+\frac{\partial f_0}{\partial\bar{\rho}_+}\right) \tag{55}$$

with respect to the density,

$$\frac{\beta}{\bar{\rho}_+\chi_P} \equiv \beta\frac{\partial P}{\partial\bar{\rho}_+} = 1 + 2\bar{\rho}_+\frac{\partial f_0}{\partial\bar{\rho}_+} + \bar{\rho}_+^2\frac{\partial^2 f_0}{\partial\bar{\rho}_+^2} = \frac{1 + 39\omega - 4\omega^3}{36\omega} \ . \tag{56}$$

For small couplings this can be expanded to yield

$$\frac{\beta}{\bar{\rho}_+\chi_P} = 1 - \frac{\sqrt{3}}{4}\Gamma^{3/2} + \frac{1}{2}\Gamma^3 - \frac{5}{2\sqrt{3}}\Gamma^{9/2} + \frac{21}{4}\Gamma^6 + \mathcal{O}(\Gamma^{13/2}) \ . \tag{57}$$

To see if our expression for $S(k)$ is consistent with the sum rules, we expand (53) around $\alpha = 0$, using the asymptotic form of the spherical Bessel function of the first kind,

$$\lim_{\alpha\to 0} j_\ell(\alpha x) = \frac{(\alpha x)^\ell}{(2\ell+1)} = \frac{(\alpha x)^\ell}{1.3.5\ldots(2\ell+1)} \ . \tag{58}$$

It is evident that, up to order $\mathcal{O}(k^0)$, only the isotropic ($\ell=0$) terms of (53) contribute to the structure factor. We find

$$S^{-1}(\boldsymbol{k}) = \left(\frac{\kappa_{\mathrm{D}}}{k}\right)^2 + \frac{\beta}{\bar{\rho}_+\chi_S} + \mathcal{O}(k^2) \ , \tag{59}$$

$$\begin{aligned}
\frac{\beta}{\bar{\rho}_+\chi_S} &= 1 - \frac{1}{12}\int_1^\omega \mathrm{d}\omega_\lambda\,\frac{(2\omega_\lambda+1)(2\omega_\lambda^2-\omega_\lambda+2)}{\omega_\lambda^2+\omega_\lambda+1} \\
&= 1 - \frac{1}{6}\left[1 - 2\omega + \omega^2 - \frac{\pi\sqrt{3}}{2} + \frac{3}{4}\ln\left(\frac{\omega^2+\omega+1}{3}\right)\right. \\
&\quad \left. + \frac{3\sqrt{3}}{2}\tan^{-1}\left(\frac{2\omega+1}{\sqrt{3}}\right)\right] \ .
\end{aligned} \tag{60}$$

In the low-density limit the inverse compressibility derived from the structure factor can be expanded to yield

$$\frac{\beta}{\bar{\rho}_+\chi_S} = 1 - \frac{\sqrt{3}}{4}\Gamma^{3/2} + \frac{1}{2}\Gamma^3 - \frac{5}{2\sqrt{3}}\Gamma^{9/2} + \frac{81}{16}\Gamma^6 + \mathcal{O}(\Gamma^{13/2}) \ . \tag{61}$$

We see that the structure factor satisfies *exactly* the charge-neutrality and the second-moment conditions, while the compressibility sum rule is satisfied only to order $\Gamma^{9/2}$. This results from the fact that, in order to simplify the calculations, we have neglected the dependence of the cavity size and shape on the imposed density variation
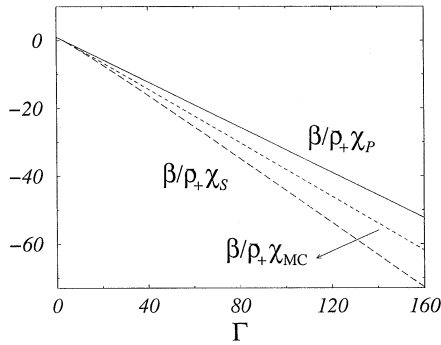
Fig. 1. Comparison between the inverse compressibilities derived from the pressure, Eq. (56), solid line ($\beta/\bar{\rho}_+\chi_{\mathrm{P}}$), and from the structure factor, Eq. (60), long-dashed line ($\beta/\bar{\rho}_+\chi_{\mathrm{S}}$). The dashed line ($\beta/\bar{\rho}_+\chi_{\mathrm{MC}}$) represents the fit of the MC data over the interval $1 \leqslant \Gamma \leqslant 160$ [27].
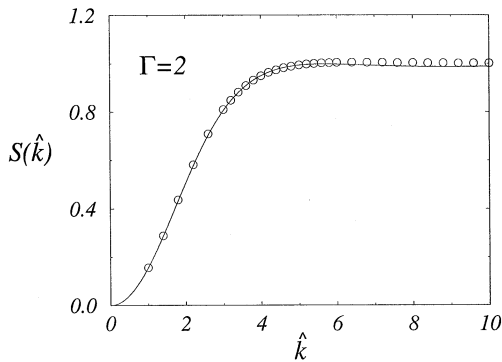

Fig. 2. Structure factor $S(\hat{k})$ for $\Gamma = 2$. The solid line is our expression (53) calculated up to $\ell = 6$, while the circles represent the MC data [28].

($\varDelta$). Clearly, if this was taken into account, the theory would be completely internally self-consistent. Nevertheless, even at this level of approximation, the lack of self-consistency is quite small over the full range of relevant coupling constants, as can be measured by the inverse compressibilities derived from the thermodynamic (χ_{P}) and the structure factor (χ_{S}) routes, Eqs. (56) and (60), respectively; see Fig. 1. The fit of the MC data [27] leads to an inverse compressibility (χ_{MC}) which is between the two previous ones.

Defining $\hat{k} \equiv kd = \alpha\sqrt{3\Gamma}$, we have explicitly carried out the summation for the first six terms of the infinite series in Eq. (53). The results for the structure factor for various values of Γ, obtained *without any fitting parameters,* are plotted in Figs. 2–5. The agreement with the MC simulations [28] is quite encouraging. We should note, however, that for higher couplings, in the vicinity of the first peak, the series is slowly convergent. This is the reason why we did not attempt to carry the calculations for $\Gamma > 40$.
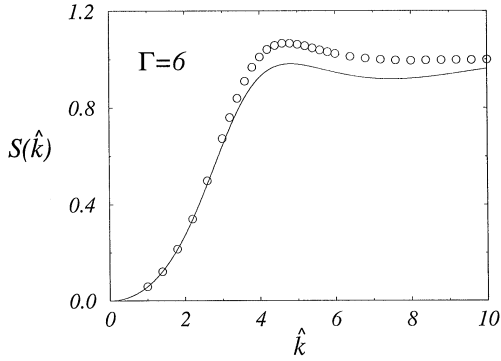
Fig. 3. Structure factor $S(\hat{k})$ for $\Gamma = 6$. The solid line is our expression (53) calculated up to $\ell = 6$, while the circles represent the MC data [28].
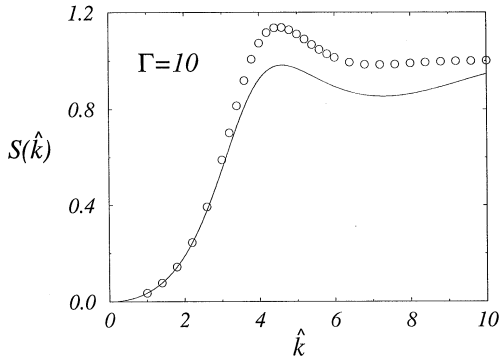

Fig. 4. Structure factor $S(\hat{k})$ for $\Gamma = 10$. The solid line is our expression (53) calculated up to $\ell = 6$, while the circles represent the MC data [28].
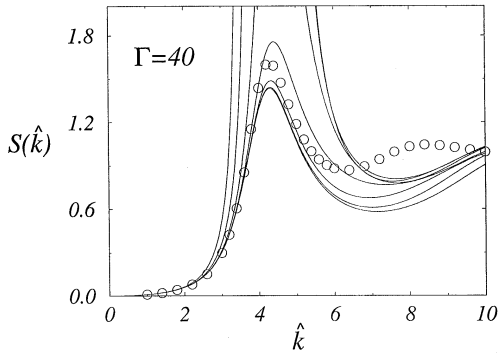

Fig. 5. Structure factor $S(\hat{k})$ for $\Gamma = 40$. The solid lines are our expression (53) with the $\ell = 0, 1, 2, \ldots$ up to the $\ell = 6$ terms included in the sum (from top to bottom). The circles represent the MC data [28]. We note that for higher values of Γ, more and more terms will need to be included in order to achieve convergence in the vicinity of the first peak.

4. Conclusions

We have presented the generalized Debye–Hückel theory of the one-component plasma. The linearity of the theory allows for explicit calculations of all the thermodynamic functions, as well as the structure factor, which is expressed as an infinite series. The linearity also insures the internal consistency of the theory. The agreement with the Monte Carlo simulations, obtained *without any fitting parameters,* is quite good, suggesting that the existence of an effective cavity surrounding each ion is theoretically justified.

Acknowledgements

Appendix A. Some useful integrals

In this appendix we present some integrals which appear along the text. We introduce the Kronecker delta,

$$\delta_{k0} = \frac{1}{V}(2\pi)^3 \delta^3(k), \tag{A.1}$$

where $V = (2\pi)^3 \delta^3(0)$ is the volume of the system and $\delta^3(k)$ is the three-dimensional Dirac delta function,

$$\delta^3(k) \equiv \left(\frac{1}{2\pi}\right)^3 \int d^3r' \exp(i k \cdot r'). \tag{A.2}$$

From the definition (A.2) of the three-dimensional Dirac delta function, it follows directly

$$\int d^3r' \cos k \cdot r' = \frac{1}{2} \int d^3r' \left[\exp(i k \cdot r') + \exp(-i k \cdot r')\right]$$

$$= \frac{1}{2}(2\pi)^3 \left[\delta^3(k) + \delta^3(-k)\right] = (2\pi)^3 \delta^3(k) = V\delta_{k0}, \tag{A.3}$$

$$\int d^3r' \cos^2 k \cdot r' = \frac{1}{2} \int d^3r' \left(1 + \cos 2k \cdot r'\right) = \frac{1}{2}\left[V + (2\pi)^3 \delta^3(2k)\right]$$

$$= \frac{V}{2}(1 + \delta_{k0}). \tag{A.4}$$

A simple generalization of (A.4) leads to

$$\int d^3r' \cos^2\left(k \cdot r' + \ell\frac{\pi}{2}\right) = \frac{V}{2}\left[1 + (-1)^\ell \delta_{k0}\right], \tag{A.5}$$

where ℓ is an integer.

Expressing $1/r$ as the inverse Fourier transform

$$\frac{1}{r} = \frac{1}{2\pi^2} \int d^3k \, \frac{1}{k^2} \exp(-i\mathbf{k} \cdot \mathbf{r}) \,, \tag{A.6}$$

we have

$$
\begin{aligned}
\int d^3r \, d^3r' \, \frac{\cos \mathbf{k} \cdot \mathbf{r} \cos \mathbf{k} \cdot \mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} &= \frac{1}{4\pi^2} \int d^3r \, d^3r' \, d^3q \, \frac{1}{q^2} \exp\left[-i\mathbf{q} \cdot (\mathbf{r} - \mathbf{r}')\right] \\
&\quad \times \left[\cos \mathbf{k} \cdot (\mathbf{r} + \mathbf{r}') + \cos \mathbf{k} \cdot (\mathbf{r} - \mathbf{r}')\right] \\
&= \frac{1}{8\pi^2} \int d^3r \, d^3r' \, d^3q \, \frac{1}{q^2} \sum_{\alpha_1 = \pm} \exp\left[i(\alpha_1 \mathbf{k} - \mathbf{q}) \cdot \mathbf{r}\right] \\
&\quad \times \sum_{\alpha_2 = \pm} \exp\left[i(\alpha_2 \mathbf{k} + \mathbf{q}) \cdot \mathbf{r}'\right] \\
&= \frac{1}{2}(2\pi)^4 \int d^3q \, \frac{1}{q^2} \sum_{\alpha_1, \alpha_2 = \pm} \delta^3\left(\alpha_1 \mathbf{k} - \mathbf{q}\right) \delta^3\left(\alpha_2 \mathbf{k} + \mathbf{q}\right) \\
&= \frac{(2\pi)^4}{k^2} \left[\delta^3(\mathbf{0}) + \frac{1}{2}\delta^3(2\mathbf{k}) + \frac{1}{2}\delta^3(-2\mathbf{k})\right] \\
&= \frac{2\pi V}{k^2} (1 + \delta_{\mathbf{k0}}) \,. \tag{A.7}
\end{aligned}
$$

Appendix B. Variation of the free-energy density

In this appendix we obtain the variation of the reduced free-energy density, $\delta f = \beta \delta F / V$, up to quadratic order in the perturbation parameter Δ.

The Helmholtz free energy F is written as a functional of the mobile-ion density $\rho_+(\mathbf{r})$. The variation δF is obtained using the functional Taylor series,

$$
\begin{aligned}
\beta \, \delta F \left[\rho_+(\mathbf{r})\right] &= \beta F \left[\rho_+(\mathbf{r})\right] - \beta F \left[\bar{\rho}_+\right] \\
&= \int d^3r' \, \left. \frac{\beta \, \delta F}{\delta \rho_+(\mathbf{r}')} \right|_{\rho_+(\mathbf{r}) = \bar{\rho}_+} \delta \rho_+(\mathbf{r}') \\
&\quad + \frac{1}{2} \int d^3r' \, d^3r'' \, \left. \frac{\beta \delta^2 F}{\delta \rho_+(\mathbf{r}') \, \delta \rho_+(\mathbf{r}'')} \right|_{\rho_+(\mathbf{r}) = \bar{\rho}_+} \delta \rho_+(\mathbf{r}') \, \delta \rho_+(\mathbf{r}'') \,.
\end{aligned}
\tag{B.1}
$$

The linear term can be written as

$$
\beta \, \delta F^{(1)} \left[\rho_+(\mathbf{r})\right] = \int d^3r' \, \left. \frac{\beta \delta F}{\delta \rho_+(\mathbf{r}')} \right|_{\rho_+(\mathbf{r}) = \bar{\rho}_+} \delta \rho_+(\mathbf{r}') = \int d^3r' \, \beta \mu(\mathbf{r}') \, \delta \rho_+(\mathbf{r}') \,,
\tag{B.2}
$$

where $\mu(\mathbf{r})$ is the chemical potential at the position $\mathbf{r}$,

$$\mu(\mathbf{r}) \equiv \left. \frac{\delta F}{\delta \rho_+(\mathbf{r})} \right|_{\rho_+(\mathbf{r}) = \bar{\rho}_+} . \tag{B.3}$$

However, at the thermodynamical equilibrium, the chemical potential of the system is constant and is independent of position,

$$\mu(\mathbf{r}) = \bar{\mu}, \qquad \forall \mathbf{r} . \tag{B.4}$$

Using the imposed variation (7) of the mobile-ion density,

$$\delta \rho_+(\mathbf{r}) = \bar{\rho}_+ \Delta \cos \mathbf{k} \cdot \mathbf{r} = \tfrac{1}{2} \bar{\rho}_+ \Delta \left[\exp(i\mathbf{k} \cdot \mathbf{r}) + \exp(-i\mathbf{k} \cdot \mathbf{r}) \right] , \tag{B.5}$$

the linear term can be expressed as

$$\beta \, \delta F^{(1)} [\rho_+(\mathbf{r})] = \beta \bar{\mu} \bar{\rho}_+ \Delta \int d^3 r' \cos \mathbf{k} \cdot \mathbf{r}' = \beta \bar{\mu} \bar{\rho}_+ V \Delta \delta_{\mathbf{k0}} . \tag{B.6}$$

The quadratic term,

$$\beta \, \delta F^{(2)} [\rho_+(\mathbf{r})] = \frac{1}{2} \int d^3 r' \, d^3 r'' \left. \frac{\beta \delta^2 F}{\delta \rho_+(\mathbf{r}') \, \delta \rho_+(\mathbf{r}'')} \right|_{\rho_+(\mathbf{r}) = \bar{\rho}_+} \delta \rho_+(\mathbf{r}') \, \delta \rho_+(\mathbf{r}'')$$

$$= \frac{1}{2} \int d^3 r' \, d^3 r'' \left[\frac{\delta (\mathbf{r}' - \mathbf{r}'')}{\bar{\rho}_+} - C_{++} (\mathbf{r}' - \mathbf{r}'') \right] \delta \rho_+(\mathbf{r}') \, \delta \rho_+(\mathbf{r}'') \tag{B.7}$$

can be split into two parts, the ideal-gas contribution,

$$\beta \, \delta F^{(2)}_{\text{ideal}} [\rho_+(\mathbf{r})] = \frac{1}{2 \bar{\rho}_+} \int d^3 r' \, d^3 r'' \, \delta(\mathbf{r}' - \mathbf{r}'') \, \delta \rho_+(\mathbf{r}') \, \delta \rho_+(\mathbf{r}'') \tag{B.8}$$

and the electrostatic contribution,

$$\beta \delta F^{(2)}_{\text{elect}} [\rho_+(\mathbf{r})] = -\frac{1}{2} \int d^3 r' \, d^3 r'' \, C_{++} (\mathbf{r}' - \mathbf{r}'') \, \delta \rho_+(\mathbf{r}') \, \delta \rho_+(\mathbf{r}'') , \tag{B.9}$$

where $C_{++} (\mathbf{r}' - \mathbf{r}'')$ is the direct correlation function.

Using (A.4) and (B.5), the ideal-gas contribution can be straightforwardly obtained,

$$\beta \, \delta F^{(2)}_{\text{ideal}} [\rho_+(\mathbf{r})] = \frac{1}{2 \bar{\rho}_+} \int d^3 r' \left[\delta \rho_+(\mathbf{r}') \right]^2 = \frac{1}{2} \bar{\rho}_+ \Delta^2 \int d^3 r' \cos^2 \mathbf{k} \cdot \mathbf{r}'$$

$$= \frac{V}{4} \bar{\rho}_+ \Delta^2 (1 + \delta_{\mathbf{k0}}) . \tag{B.10}$$

To evaluate the electrostatic contribution we use (B.5), and express $C_{++} (\mathbf{r}' - \mathbf{r}'')$ as the inverse Fourier transform

$$C_{++} (\mathbf{r}) = \left(\frac{1}{2\pi} \right)^3 \int d^3 k \, \hat{C}_{++}(\mathbf{k}) \exp(-i\mathbf{k} \cdot \mathbf{r}) , \tag{B.11}$$

leading to

$$\beta \, \delta F_{\text{elect}}^{(2)} \left[\rho_+(\mathbf{r}) \right] = -\frac{1}{8} \bar{\rho}_+^2 \, \Delta^2 \left(\frac{1}{2\pi} \right)^3 \int \mathrm{d}^3 \mathbf{r}' \, \mathrm{d}^3 \mathbf{r}'' \, \mathrm{d}^3 \mathbf{q} \, \hat{C}_{++}(\mathbf{q})$$

$$\times \sum_{\alpha_1 = \pm} \exp\left[\mathrm{i}(\alpha_1 \mathbf{k} - \mathbf{q}) \cdot \mathbf{r}' \right] \sum_{\alpha_2 = \pm} \exp\left[\mathrm{i}(\alpha_2 \mathbf{k} + \mathbf{q}) \cdot \mathbf{r}'' \right]$$

$$= -\frac{1}{8} \bar{\rho}_+^2 \, \Delta^2 \, (2\pi)^3 \int \mathrm{d}^3 \mathbf{q} \, \hat{C}_{++}(\mathbf{q}) \sum_{\alpha_1, \alpha_2 = \pm} \delta^3 \left(\alpha_1 \mathbf{k} - \mathbf{q} \right) \delta^3 \left(\alpha_2 \mathbf{k} + \mathbf{q} \right)$$

$$= -\frac{1}{8} \bar{\rho}_+^2 \, \Delta^2 \, (2\pi)^3 \left\{ \hat{C}_{++}(\mathbf{k}) \left[\delta^3 (\mathbf{0}) + \delta^3 (2\mathbf{k}) \right] \right.$$

$$\left. + \hat{C}_{++}(-\mathbf{k}) \left[\delta^3 (\mathbf{0}) + \delta^3 (-2\mathbf{k}) \right] \right\}$$

$$= -\frac{V}{4} \hat{C}_{++}(\mathbf{k}) \bar{\rho}_+^2 \Delta^2 \left(1 + \delta_{\mathbf{k0}} \right) , \tag{B.12}$$

where we have used the symmetry of the direct correlation function, $\hat{C}_{++}(\mathbf{k}) = \hat{C}_{++}(-\mathbf{k})$. Combining all the pieces, the variation of the reduced free-energy density can be written as

$$\delta f \left[\rho_+(\mathbf{r}) \right] = \frac{\beta}{V} \delta F^{(1)} \left[\rho_+(\mathbf{r}) \right] + \frac{\beta}{V} \delta F_{\text{ideal}}^{(2)} \left[\rho_+(\mathbf{r}) \right] + \frac{\beta}{V} \delta F_{\text{elect}}^{(2)} \left[\rho_+(\mathbf{r}) \right]$$

$$= \beta \bar{\mu} \bar{\rho}_+ \Delta \delta_{\mathbf{k0}} + \frac{1}{4} \left[1 - \bar{\rho}_+ \hat{C}_{++}(\mathbf{k}) \right] \bar{\rho}_+ \Delta^2 \left(1 + \delta_{\mathbf{k0}} \right)$$

$$= \beta \bar{\mu} \bar{\rho}_+ \Delta \delta_{\mathbf{k0}} + \frac{1}{4} S^{-1}(\mathbf{k}) \bar{\rho}_+ \Delta^2 \left(1 + \delta_{\mathbf{k0}} \right) , \tag{B.13}$$

where $S(\mathbf{k})$ is the structure factor. Note that the linear contribution to the variation has a Kronecker delta ($\delta_{\mathbf{k0}}$) factor, which expresses the translational invariance (B.3) of the equilibrium chemical potential $\bar{\mu}$ of the system.

Appendix C. Green's function associated with the induced potential

In this appendix we obtain the Green's function associated with the differential equation satisfied by the induced potential $\tilde{\phi}(\mathbf{r}, \mathbf{r}')$.

The Green's function $G(\mathbf{R}, \mathbf{R}')$ associated with (31), where $\mathbf{R} = \mathbf{r} - \mathbf{r}'$, satisfies the homogeneous equation [17,18]

$$\left[\nabla_R^2 - \kappa_{\text{D}}^2 \Theta(|\mathbf{R}| - h) \right] G(\mathbf{R}, \mathbf{R}') = -4\pi \delta^3(\mathbf{R} - \mathbf{R}')$$

$$= -\frac{4\pi}{R^2} \delta(R - R') \, \delta(\cos\theta - \cos\theta') \, \delta(\varphi - \varphi') \tag{C.1}$$

with $\Theta(\xi)$ the Heaviside step function.

The general solution of (C.1) can be written as [9]

$$G\left(\mathbf{R}, \mathbf{R}'\right) = \kappa_{\mathrm{D}} \sum_{\ell=0}^{\infty} G_\ell\left(\kappa_{\mathrm{D}} R, \kappa_{\mathrm{D}} R'\right) P_\ell\left(\frac{\mathbf{R} \cdot \mathbf{R}'}{R R'}\right) , \tag{C.2}$$

where $P_\ell(\xi)$ denotes a Legendre polynomial.

Replacing (C.2) into (C.1), multiplying both sides by $P_{\ell'}\left(\mathbf{R} \cdot \mathbf{R}'/R R'\right)$ and integrating over the angular coordinates θ and φ, we obtain the equation satisfied by the radial functions $G_\ell(s, s')$,

$$\left[\frac{\mathrm{d}^2}{\mathrm{d}s^2} + \frac{2}{s}\frac{\mathrm{d}}{\mathrm{d}s} - \Theta(s - x) - \frac{\ell(\ell+1)}{s^2}\right] G_\ell\left(s, s'\right) = -\frac{1}{s^2}(2\ell+1)\,\delta(s - s') , \tag{C.3}$$

where we have introduced the adimensional variables $s = \kappa_{\mathrm{D}} R$, $s' = \kappa_{\mathrm{D}} R'$ and $x = \kappa_{\mathrm{D}} h$. To obtain (C.3) we have used the property of the Dirac delta function,

$$\delta(\kappa_{\mathrm{D}} R - \kappa_{\mathrm{D}} R') = \frac{1}{\kappa_{\mathrm{D}}}\delta(R - R') , \tag{C.4}$$

the addition theorem for the Legendre polynomials,

$$\begin{aligned} P_\ell\left(\frac{\mathbf{R} \cdot \mathbf{R}'}{R R'}\right) &= P_\ell\left[\cos\theta \cos\theta' + \sin\theta \sin\theta' \cos(\varphi - \varphi')\right] \\ &= P_\ell(\cos\theta) P_\ell(\cos\theta') + 2\sum_{m=1}^{\ell} \frac{(\ell - m)!}{(\ell + m)!} \\ &\quad \times P_\ell^m\left(\cos\theta\right) P_\ell^m\left(\cos\theta'\right) \cos m(\varphi - \varphi') \end{aligned} \tag{C.5}$$

and their orthogonality,

$$\int_{-1}^{1} \mathrm{d}(\cos\theta)\, P_\ell(\cos\theta)\, P_{\ell'}(\cos\theta) = \frac{2}{2\ell+1}\delta_{\ell\ell'} . \tag{C.6}$$

The solutions of (C.3) that are finite for $s \to 0$ and vanish as $s \to \infty$ can be written as

$$G_\ell\left(s, s'\right) = \begin{cases} A_{11}s^\ell & \text{for } 0 < s < s' < x, \\ A_{12}s^\ell + A_{13}s^{-(\ell+1)} & \text{for } 0 < s' < s < x, \\ A_{21}s^\ell & \text{for } 0 < s < x < s', \\ A_{22}k_\ell(s) & \text{for } 0 < s' < x < s, \\ A_{31}k_\ell(s) & \text{for } 0 < x < s' < s, \\ A_{32}i_\ell(s) + A_{33}k_\ell(s) & \text{for } 0 < x < s < s', \end{cases} \tag{C.7}$$

where the coefficients $\{A_{mn}\}$ are functions of x and s' to be determined by the boundary conditions; $i_\ell(s)$ and $k_\ell(s)$ are the modified spherical Bessel functions of the first and the third kinds [16], respectively,

$$i_\ell(s) = \sqrt{\frac{\pi}{2s}}\, I_{\ell+1/2}(s) , \tag{C.8}$$

$$k_\ell(s) = \sqrt{\frac{2}{\pi s}}\, K_{\ell+1/2}(s) . \tag{C.9}$$

Using the symmetry property of the Green's function [31], we can rewrite Eqs. (C.7) as

$$G_\ell^{(1)}(s,s') = A_1 s^\ell s'^\ell + B_1 \frac{s_<^\ell}{s_>^{\ell+1}} \qquad \text{for } 0 < s,s' < x \,, \tag{C.10}$$

$$G_\ell^{(2)}(s,s') = A_2 s_<^\ell k_\ell(s_>) \qquad \text{for } 0 < s_< < x < s_> \,, \tag{C.11}$$

$$G_\ell^{(3)}(s,s') = A_3 k_\ell(s) k_\ell(s') + B_3 i_\ell(s_<) k_\ell(s_>) \qquad \text{for } 0 < x < s,s' \,, \tag{C.12}$$

where $s_< = \min(s,s')$, $s_> = \max(s,s')$, and the coefficients $\{A_n, B_n\}$ depend now only on the size of the exclusion hole x.

The coefficients $\{B_n\}, n = 1,3$, are obtained by imposing the discontinuity of the derivative of $G_\ell(s,s')$ associated with the Dirac delta function,

$$\frac{\mathrm{d}}{\mathrm{d}s}\left[s G_\ell^{(n)}(s,s') \right]_{s=s'+\varepsilon} - \frac{\mathrm{d}}{\mathrm{d}s}\left[s G_\ell^{(n)}(s,s') \right]_{s=s'-\varepsilon} = -\frac{2\ell+1}{s'} \,, \tag{C.13}$$

where ε is a positive infinitesimal. Using the Wronskian of the modified spherical Bessel functions [29,30],

$$W[k_\ell(s), i_\ell(s)] = k_\ell(s) i_\ell'(s) - i_\ell(s) k_\ell'(s) = \frac{1}{s^2} \,, \tag{C.14}$$

this leads to

$$B_1 = 1 \,, \tag{C.15}$$

$$B_3 = 2\ell + 1 \,. \tag{C.16}$$

The coefficients $\{A_n\}, n = 1,2,3$, are obtained by imposing the continuity of $G_\ell(s,s')$ and of its derivative across the spherical surface at $s = s' = x$,

$$G_\ell^{(1)}(s,s')\Big|_{s=s'=x} = G_\ell^{(2)}(s,s')\Big|_{s=s'=x} = G_\ell^{(3)}(s,s')\Big|_{s=s'=x} \,, \tag{C.17}$$

$$\frac{\mathrm{d}}{\mathrm{d}s} G_\ell^{(1)}(s,s')\Big|_{s=s'+\varepsilon=x} = \frac{\mathrm{d}}{\mathrm{d}s} G_\ell^{(2)}(s,s')\Big|_{s=s'+\varepsilon=x} \,, \tag{C.18}$$

and using the following relations of the modified spherical Bessel functions [29,30] to express $i_\ell(x)$, $k_\ell(x)$ and $k_\ell'(x)$ in terms of $i_{\ell\pm1}(x)$ and $k_{\ell\pm1}(x)$:

$$\frac{1}{x^2} = i_{\ell+1}(x) k_\ell(x) + k_{\ell+1}(x) i_\ell(x) \,, \tag{C.19}$$

$$(2\ell+1) k_\ell(x) = x k_{\ell+1}(x) - x k_{\ell-1}(x) \,, \tag{C.20}$$

$$-(2\ell+1) k_\ell'(x) = \ell k_{\ell-1}(x) + (\ell+1) k_{\ell+1}(x) \,, \tag{C.21}$$

which yield

$$A_1 = -\frac{k_{\ell-1}(x)}{x^{2\ell+1} k_{\ell+1}(x)} \,, \tag{C.22}$$

$$A_2 = \frac{2\ell + 1}{x^{\ell+2} k_{\ell+1}(x)} \,, \tag{C.23}$$

$$A_3 = (2\ell + 1) \frac{i_{\ell+1}(x)}{k_{\ell+1}(x)} \,. \tag{C.24}$$

Therefore, the Green's function $G(\boldsymbol{R}, \boldsymbol{R}')$ is given by expansion (C.2), with the radial functions $G_\ell(s, s')$ defined by [17,18]

$$G_\ell^{(1)}(s, s') = \frac{s_<^\ell}{s_>^{\ell+1}} - \frac{s^\ell s'^\ell k_{\ell-1}(x)}{x^{2\ell+1} k_{\ell+1}(x)} \quad \text{for } 0 < s, s' < x \,, \tag{C.25}$$

$$G_\ell^{(2)}(s, s') = (2\ell + 1) \frac{s_<^\ell k_\ell(s_>)}{x^{\ell+2} k_{\ell+1}(x)} \quad \text{for } 0 < s_< < x < s_> \,, \tag{C.26}$$

$$G_\ell^{(3)}(s, s') = (2\ell + 1) \left[\frac{i_{\ell+1}(x)}{k_{\ell+1}(x)} k_\ell(s) k_\ell(s') + i_\ell(s_<) k_\ell(s_>) \right] \quad \text{for } 0 < x < s, s' \,. \tag{C.27}$$

Appendix D. The perturbative solution of the induced potential

In this appendix we obtain the induced potential $\tilde{\phi}(\boldsymbol{r}, \boldsymbol{r}')$ recursively, up to order $\varDelta^2$, at the center of the exclusion hole, $|\boldsymbol{r} - \boldsymbol{r}'| = 0$.

Let us obtain the induced potential *outside* the exclusion hole, $|\boldsymbol{r} - \boldsymbol{r}'| \geqslant h$, which we will denote by $\tilde{\phi}_>(\boldsymbol{r}, \boldsymbol{r}')$. Clearly, this potential is produced by the charge distribution inside and outside the cavity. Let us first calculate the contribution to the potential arising from the charge *inside* the hole, $\tilde{\phi}_>^{(<)}(\boldsymbol{r}, \boldsymbol{r}')$. Since our final goal is to calculate the potential at the center of the cavity to order $\varDelta^2$, it is sufficient to calculate the induced potential *outside* the hole to order $\varDelta$, see Eq. (33). Using the Green's function $G(\boldsymbol{R}, \boldsymbol{R}')$ derived in appendix C, where $\boldsymbol{R} = \boldsymbol{r} - \boldsymbol{r}'$, we find to first order in $\varDelta$,

$$\begin{aligned}
\tilde{\phi}_>^{(<)}(\boldsymbol{r}, \boldsymbol{r}') &= \tilde{\phi}_>^{(<)}(\boldsymbol{R} + \boldsymbol{r}', \boldsymbol{r}') = \frac{1}{D} \int_{|\boldsymbol{R}'| \leqslant h} d^3 \boldsymbol{R}' \, \varrho(\boldsymbol{R}') \, G(\boldsymbol{R}, \boldsymbol{R}') \\
&= \frac{q \kappa_D}{D} \int_{|\boldsymbol{R}'| \leqslant h} d^3 \boldsymbol{R}' \left\{ \delta^3(\boldsymbol{R}') - \bar{\rho}_+ \left[1 + \varDelta \cos \boldsymbol{k} \cdot (\boldsymbol{R}' + \boldsymbol{r}') \right] \right\} \\
&\quad \times \sum_{\ell=0}^\infty P_\ell \left(\frac{\boldsymbol{R} \cdot \boldsymbol{R}'}{R R'} \right) \\
&= \frac{1}{\beta q} \left(\lambda_B \kappa_D - \frac{1}{3} x^3 \right) \frac{k_0(\kappa_D R)}{x^2 k_1(x)} - \frac{q \bar{\rho}_+ \kappa_D}{D} \varDelta \mathrm{Re} \left[\exp(i \boldsymbol{k} \cdot \boldsymbol{r}') \sum_{\ell=0}^\infty (2\ell + 1) \right. \\
&\quad \left. \times \frac{k_\ell(\kappa_D R)}{x^{\ell+2} k_{\ell+1}(x)} \int_{|\boldsymbol{R}'| \leqslant h} d^3 \boldsymbol{R}' \, (\kappa_D R')^\ell \exp(i \boldsymbol{k} \cdot \boldsymbol{R}') P_\ell \left(\frac{\boldsymbol{R} \cdot \boldsymbol{R}'}{R R'} \right) \right] \,,
\end{aligned} \tag{D.1}$$

recalling that $x = \kappa_D h$. The first term of (D.1) can be simplified using the identities

$$k_1(x) = (1 + x) \frac{e^{-x}}{x^2} \, , \tag{D.2}$$

$$\lambda_B \kappa_D = \tfrac{1}{3} \left[(1 + x)^3 - 1 \right] = x(1 + x) + \tfrac{1}{3} x^3 \, . \tag{D.3}$$

Relation (D.3) is the defining equation for the cavity size, x, Eq. (5). It is important to remember that it does not take into account the imposed variation in the ionic density, and as result will be responsible for the violation of the compressibility sum rule.

To simplify the second term of (D.1), we note first that, without loss of generality, we can choose the z-axis along the k direction,

$$\cos\theta = \frac{k \cdot R}{kR}, \qquad \cos\theta' = \frac{k \cdot R'}{kR'} \, , \tag{D.4}$$

$$\tan\varphi = \frac{R \cdot \hat{y}}{R \cdot \hat{x}} \, , \qquad \tan\varphi' = \frac{R' \cdot \hat{y}}{R' \cdot \hat{x}} \, , \tag{D.5}$$

so that the addition theorem for the Legendre polynomials can be written as

$$P_\ell \left(\frac{R \cdot R'}{RR'} \right) = P_\ell \left[\cos\theta\cos\theta' + \sin\theta\sin\theta'\cos(\varphi - \varphi') \right]$$

$$= P_\ell(\cos\theta)P_\ell(\cos\theta') + 2\sum_{m=1}^{\ell} \frac{(\ell - m)!}{(\ell + m)!}$$

$$\times P_\ell^m(\cos\theta)P_\ell^m(\cos\theta')\cos m(\varphi - \varphi') \, . \tag{D.6}$$

Performing the integrations over the azimuthal angle φ', only the $m = 0$ terms survive,

$$\tilde{\phi}_>^{(<)}(r, r') = \frac{1}{\beta q} x e^x k_0(\kappa_D R) - \frac{\kappa_D^3}{\beta q} \varDelta \, \mathrm{Re} \left[\exp(ik \cdot r') \sum_{\ell=0}^{\infty} (2\ell + 1) \frac{k_\ell(\kappa_D R)}{x^{\ell+2} k_{\ell+1}(x)} \right.$$

$$\times P_\ell(\cos\theta) \int_0^h dR' \, R'^2 \, (\kappa_D R')^\ell$$

$$\left. \times \int_{-1}^{1} d(\cos\theta')\exp(ikR'\cos\theta') \, P_\ell(\cos\theta') \right] \, . \tag{D.7}$$

To proceed, we use the plane-wave expansion,

$$\exp(ikR'\cos\theta') = \sum_{\ell=0}^{\infty} (2\ell + 1) \, i^\ell j_\ell(kR')P_\ell(\cos\theta') \, , \tag{D.8}$$

where $j_\ell(\xi)$ is the spherical Bessel function of the first kind,

$$j_\ell(\xi) = \sqrt{\frac{\pi}{2\xi}} \, J_{\ell+1/2}(\xi) \, . \tag{D.9}$$

The integrations over the polar angle θ' and over the radial coordinate R' can be performed using the orthogonality of the Legendre polynomials,

$$\int_{-1}^{1} d(\cos\theta') P_\ell(\cos\theta') P_{\ell'}(\cos\theta') = \frac{2}{2\ell + 1} \delta_{\ell\ell'} \tag{D.10}$$

and the recursion relation for the spherical Bessel function of the first kind,

$$\frac{\mathrm{d}}{\mathrm{d}\xi}\left[\xi^{\ell+2}j_{\ell+1}(\xi)\right] = \xi^{\ell+2}j_\ell(\xi)\,, \tag{D.11}$$

which yields

$$\begin{aligned}
\tilde{\phi}_>^{(<)}(\boldsymbol{r},\boldsymbol{r}') = \tilde{\phi}_>^{(<)}(\boldsymbol{R}+\boldsymbol{r}',\boldsymbol{r}') = {}&\frac{1}{\beta q}x\mathrm{e}^x k_0(\kappa_\mathrm{D}R)\\
&-\frac{1}{\alpha\beta q}\Delta\sum_{\ell=0}^\infty (2\ell+1)\cos\left(\boldsymbol{k}\cdot\boldsymbol{r}'+\ell\frac{\pi}{2}\right)\\
&\times\frac{j_{\ell+1}(\alpha x)}{k_{\ell+1}(x)}k_\ell(\kappa_\mathrm{D}R)\,P_\ell(\cos\theta)\,,
\end{aligned} \tag{D.12}$$

where $\alpha = k/\kappa_\mathrm{D}$.

Substituting $\tilde{\phi}_>^{(<)}(\boldsymbol{r},\boldsymbol{r}')$ into the expression for the charge density *outside* the exclusion hole, Eq. (33), we can now calculate the contribution to the potential *outside* the exclusion hole arising from the *external* charge, $\tilde{\phi}_>^{(>)}(\boldsymbol{r},\boldsymbol{r}')$. To order Δ we find

$$\begin{aligned}
\tilde{\phi}_>^{(>)}(\boldsymbol{r},\boldsymbol{r}') = \tilde{\phi}_>^{(>)}(\boldsymbol{R}+\boldsymbol{r}',\boldsymbol{r}') = {}&\frac{1}{D}\int_{|\boldsymbol{R}'|\geqslant h}\mathrm{d}^3\boldsymbol{R}'\,\varrho\left(\boldsymbol{R}'\right)G\left(\boldsymbol{R},\boldsymbol{R}'\right)\\
= {}&-\frac{\kappa_\mathrm{D}^3}{4\pi}\Delta\int_{|\boldsymbol{R}'|\geqslant h}\mathrm{d}^3\boldsymbol{R}'\,\tilde{\phi}_>^{(<)}(\boldsymbol{R}'+\boldsymbol{r}',\boldsymbol{r}')\cos\boldsymbol{k}\cdot\left(\boldsymbol{R}'+\boldsymbol{r}'\right)\\
&\times\sum_{\ell=0}^\infty G_\ell^{(3)}(\kappa_\mathrm{D}R,\kappa_\mathrm{D}R')P_\ell\left(\frac{\boldsymbol{R}\cdot\boldsymbol{R}'}{RR'}\right)\\
= {}&-\frac{1}{\beta q}x\mathrm{e}^x\Delta\sum_{\ell=0}^\infty(2\ell+1)\cos\left(\boldsymbol{k}\cdot\boldsymbol{r}'+\ell\frac{\pi}{2}\right)\Xi_\ell(\kappa_\mathrm{D}R,\alpha)P_\ell(\cos\theta)\,,
\end{aligned} \tag{D.13}$$

where the function $\Xi_\ell(s,\alpha)$ is defined by

$$\begin{aligned}
\Xi_\ell(s,\alpha) = {}&\int_x^\infty \mathrm{d}s'\,s'^2\,k_0(s')\frac{G_\ell^{(3)}(s,s')}{2\ell+1}\,j_\ell(\alpha s')\\
= {}&\frac{i_{\ell+1}(x)}{k_{\ell+1}(x)}k_\ell(s)\int_x^\infty \mathrm{d}\xi\,\xi^2 k_0(\xi)k_\ell(\xi)j_\ell(\alpha\xi)+k_\ell(s)\\
&\times\int_x^s \mathrm{d}\xi\,\xi^2 k_0(\xi)i_\ell(\xi)j_\ell(\alpha\xi)+i_\ell(s)\int_s^\infty \mathrm{d}\xi\,\xi^2 k_0(\xi)k_\ell(\xi)j_\ell(\alpha\xi)\,.
\end{aligned} \tag{D.14}$$

We are now able to find the induced potential *inside* the exclusion hole, $|\boldsymbol{r}-\boldsymbol{r}'|\leqslant h$, up to order Δ^2,

$$\begin{aligned}
\tilde{\phi}_<(\boldsymbol{r},\boldsymbol{r}') = \tilde{\phi}_<(\boldsymbol{R}+\boldsymbol{r}',\boldsymbol{r}') = {}&\frac{1}{D}\int\mathrm{d}^3\boldsymbol{R}'\,\varrho\left(\boldsymbol{R}'\right)G\left(\boldsymbol{R},\boldsymbol{R}'\right)\\
= {}&\frac{q\kappa_\mathrm{D}}{D}\int_{|\boldsymbol{R}'|\leqslant h}\mathrm{d}^3\boldsymbol{R}'\left\{\delta^3(\boldsymbol{R}')-\bar{\rho}_+\left[1+\Delta\cos\boldsymbol{k}\cdot(\boldsymbol{R}'+\boldsymbol{r}')\right]\right\}
\end{aligned}$$

$$\times \sum_{\ell=0}^{\infty} G_\ell^{(1)}(\kappa_D R, \kappa_D R') P_\ell \left(\frac{\boldsymbol{R} \cdot \boldsymbol{R}'}{RR'} \right) - \frac{\kappa_D^3}{4\pi} \Delta \int_{|\boldsymbol{R}'| \geqslant h} \mathrm{d}^3 \boldsymbol{R}' \, \tilde{\phi}_>(\boldsymbol{R}' + \boldsymbol{r}', \boldsymbol{r}')$$

$$\times \cos \boldsymbol{k} \cdot (\boldsymbol{R}' + \boldsymbol{r}') \sum_{\ell=0}^{\infty} G_\ell^{(2)}(\kappa_D R, \kappa_D R') P_\ell \left(\frac{\boldsymbol{R} \cdot \boldsymbol{R}'}{RR'} \right) , \tag{D.15}$$

where the induced potential *outside* the exclusion hole, up to order Δ, is given by

$$\tilde{\phi}_>(\boldsymbol{r}, \boldsymbol{r}') = \tilde{\phi}_>^{(<)}(\boldsymbol{r}, \boldsymbol{r}') + \tilde{\phi}_>^{(>)}(\boldsymbol{r}, \boldsymbol{r}') . \tag{D.16}$$

Since we need just the mean induced electrostatic potential $\psi(\boldsymbol{r}')$ felt by the positive ion fixed at $\boldsymbol{r}'$, that is, at the center of the exclusion hole, $\boldsymbol{R} = \boldsymbol{0}$, and recalling that $G_\ell(\kappa_D R = 0, \kappa_D R') = 0, \forall \ell > 0$, only the isotropic ($\ell = 0$) terms of (D.15) contribute,

$$\psi(\boldsymbol{r}') = \lim_{\boldsymbol{R} \to \boldsymbol{0}} \left[\tilde{\phi}_<(\boldsymbol{R} + \boldsymbol{r}', \boldsymbol{r}') - \frac{q}{DR} \right]$$

$$= \lim_{R \to 0} \left[\frac{q\kappa_D}{D} \int_{|\boldsymbol{R}'| \leqslant h} \mathrm{d}^3 \boldsymbol{R}' \, G_0^{(1)}(\kappa_D R, \kappa_D R') \delta^3(\boldsymbol{R}') - \frac{q}{DR} \right]$$

$$- \frac{q \bar{\rho}_+ \kappa_D}{D} \int_{|\boldsymbol{R}'| \leqslant h} \mathrm{d}^3 \boldsymbol{R}' \, G_0^{(1)}(0, \kappa_D R') \left[1 + \Delta \cos \boldsymbol{k} \cdot (\boldsymbol{R}' + \boldsymbol{r}') \right]$$

$$- \frac{\kappa_D^3}{4\pi} \Delta \int_{|\boldsymbol{R}'| \geqslant h} \mathrm{d}^3 \boldsymbol{R}' \, G_0^{(2)}(0, \kappa_D R') \tilde{\phi}_>(\boldsymbol{R}' + \boldsymbol{r}', \boldsymbol{r}') \cos \boldsymbol{k} \cdot (\boldsymbol{R}' + \boldsymbol{r}')$$

$$= \lim_{R \to 0} \left[\frac{q\kappa_D}{D} G_0^{(1)}(\kappa_D R, 0) - \frac{q}{DR} \right] - \frac{\kappa_D^3}{\beta q} \int_0^h \mathrm{d}R' \, R'^2 G_0^{(1)}(0, \kappa_D R')$$

$$- \frac{\kappa_D^3}{\beta q} \Delta \cos \boldsymbol{k} \cdot \boldsymbol{r}' \int_0^h \mathrm{d}R' \, R'^2 G_0^{(1)}(0, \kappa_D R') j_0(kR')$$

$$- \frac{\kappa_D^3}{4\pi} \frac{1}{x^2 k_1(x)} \Delta \int_{|\boldsymbol{R}'| \geqslant h} \mathrm{d}^3 \boldsymbol{R}' \, k_0(\kappa_D R') \tilde{\phi}_>(\boldsymbol{R}' + \boldsymbol{r}', \boldsymbol{r}') \cos \boldsymbol{k} \cdot (\boldsymbol{R}' + \boldsymbol{r}') . \tag{D.17}$$

Using the explicit form of $G_0^{(1)}(s, s')$ and $\tilde{\phi}_>(\boldsymbol{r}, \boldsymbol{r}')$, and performing the angular integrations, we obtain

$$\beta q \psi(\boldsymbol{r}') = -\lambda_B \kappa_D \frac{k_{-1}(x)}{x k_1(x)} - \int_0^x \mathrm{d}s \, s^2 \left[\frac{1}{s} - \frac{k_{-1}(x)}{x k_1(x)} \right]$$

$$- \Delta \cos \boldsymbol{k} \cdot \boldsymbol{r}' \left\{ \int_0^x \mathrm{d}s \, s^2 \left[\frac{1}{s} - \frac{k_{-1}(x)}{x k_1(x)} \right] j_0(\alpha s) \right.$$

$$\left. + \frac{x e^{2x}}{1 + x} \int_x^\infty \mathrm{d}s \, s^2 k_0^2(s) j_0(\alpha s) \right\} + \frac{e^x}{\alpha(1 + x)} \Delta^2$$

$$\times \sum_{\ell=0}^{\infty} (2\ell + 1) \cos^2 \left(\boldsymbol{k} \cdot \boldsymbol{r}' + \ell \frac{\pi}{2} \right) \frac{j_{\ell+1}(\alpha x)}{k_{\ell+1}(x)}$$

$$\times \int_x^\infty \mathrm{d}s\, s^2 k_0(s) k_\ell(s) j_\ell(\alpha s) + \frac{x \mathrm{e}^{2x}}{1+x} \Delta^2 \sum_{\ell=0}^\infty (2\ell+1) \cos^2\left(\boldsymbol{k}\cdot\boldsymbol{r}' + \ell\frac{\pi}{2}\right)$$

$$\times \int_x^\infty \mathrm{d}s\, s^2 k_0(s) \Xi_\ell(s,\alpha) j_\ell(\alpha s) \,. \tag{D.18}$$

The first terms of (D.18) can be simplified using (D.2) and (D.3), supplemented by the identities

$$k_0(x) = \frac{\mathrm{e}^{-x}}{x}\,, \tag{D.19}$$

$$\frac{k_{-1}(x)}{k_1(x)} = \frac{k_1(x) - k_0(x)/x}{k_1(x)} = \frac{x}{1+x}\,, \tag{D.20}$$

$$j_0(\xi) = \frac{\sin\xi}{\xi}\,. \tag{D.21}$$

Furthermore, expressing $i_\ell(\xi)$ in terms of $k_\ell(\xi)$ using the relation [29,30]

$$i_\ell(\xi) = -\tfrac{1}{2}\left[k_\ell(-\xi) + (-1)^\ell k_\ell(\xi)\right]\,, \tag{D.22}$$

and defining the ℓth grade polynomial $g_\ell(\xi)$ associated with the modified spherical Bessel function of the third kind $k_\ell(\xi)$ by the identity [29,30]

$$g_\ell(\xi) \equiv \mathrm{e}^\xi \xi^{\ell+1} k_\ell(\xi) = \sum_{m=0}^\ell \frac{\Gamma(\ell+m+1)}{2^m m!\,\Gamma(\ell-m+1)} \xi^{\ell-m} = \sum_{m=0}^\ell \frac{(2m)!}{2^m m!} \binom{\ell+m}{2m} \xi^{\ell-m}\,, \tag{D.23}$$

where $\Gamma(m) = (m-1)!$ is the Euler gamma function, it is possible to express the last integral of (D.18), which is two-dimensional, in terms of one-dimensional quadratures,

$$\int_x^\infty \mathrm{d}s\, s^2 k_0(s) \Xi_\ell(s,\alpha) j_\ell(\alpha s) = \mathrm{e}^{-2x} (-1)^{\ell+1} \left\{ \frac{1}{2} \frac{g_{\ell+1}(-x)}{g_{\ell+1}(x)} \left[\mathscr{I}_\ell^+(x,\alpha)\right]^2 \right.$$

$$\left. + \mathscr{I}_\ell^+(x,\alpha) \mathscr{I}_\ell^-(x,\alpha) - \mathscr{I}_\ell^0(x,\alpha) \right\}\,, \tag{D.24}$$

where $\{\mathscr{I}_\ell^\nu\}, \nu = \pm, 0$, are the one-dimensional integrals

$$\mathscr{I}_\ell^-(s,\alpha) = \int_0^s \mathrm{d}\xi\, \xi^{-\ell} g_\ell(-\xi) j_\ell(\alpha\xi)\,, \tag{D.25}$$

$$\mathscr{I}_\ell^0(x,\alpha) = \int_x^\infty \mathrm{d}s\, s^{-\ell} g_\ell(s) j_\ell(\alpha s) \mathscr{I}_\ell^-(s,\alpha) \exp\left[2(x-s)\right]\,, \tag{D.26}$$

$$\mathscr{I}_\ell^+(x,\alpha) = \int_x^\infty \mathrm{d}s\, s^{-\ell} g_\ell(s) j_\ell(\alpha s) \exp\left[2(x-s)\right]\,. \tag{D.27}$$

We stress that the functions $\{\mathscr{I}_\ell^0(x,\alpha)\}$ represent one-dimensional quadratures, since the integrals $\{\mathscr{I}_\ell^-(s,\alpha)\}$ can be expressed in explicit form, for all values of ℓ, in terms of trigonometric functions and of the sine integral,

$$\mathrm{Si}\,(t) = \int_0^t \mathrm{d}\xi\, \frac{\sin\xi}{\xi}\,. \tag{D.28}$$

To illustrate, we give the three first integrals:

$$\mathscr{I}_0^-(s,\alpha) = \frac{\mathrm{Si}(\alpha s)}{\alpha}\,, \tag{D.29}$$

$$\mathscr{I}_1^-(s,\alpha) = -\frac{1}{\alpha} + \frac{\cos \alpha s}{2\alpha s} + \left(\frac{1}{\alpha^2 s} - \frac{1}{2\alpha^2 s^2}\right)\sin \alpha s + \frac{1}{2}\mathrm{Si}(\alpha s)\,, \tag{D.30}$$

$$\mathscr{I}_2^-(s,\alpha) = -1 + \left(\frac{3}{2\alpha^2 s} - \frac{3}{\alpha^2 s^2} + \frac{9}{4\alpha^2 s^3} + \frac{3}{8s}\right)\cos \alpha s$$
$$+ \left(-\frac{3}{2\alpha^3 s^2} + \frac{3}{\alpha^3 s^3} - \frac{9}{4\alpha^3 s^4} + \frac{3}{8\alpha s^2}\right)\sin \alpha s + \left(\frac{1}{2\alpha} + \frac{3\alpha}{8}\right)\mathrm{Si}(\alpha s)\,. \tag{D.31}$$

Therefore, the final form for the mean induced electrostatic potential at the center of the exclusion hole (in unities of βq) reads

$$\beta q \psi(\mathbf{r}') = -\frac{1}{2}x(x+2) - \Delta\cos \mathbf{k}\cdot\mathbf{r}'\left[\frac{1}{\alpha^2} - \frac{\sin \alpha x}{\alpha^3(1+x)} - \frac{\cos \alpha x}{\alpha^2(1+x)} + \frac{x}{1+x}\mathscr{I}_0^+(x,\alpha)\right]$$
$$+ \frac{1}{\alpha(1+x)}\Delta^2 \sum_{\ell=0}^{\infty}(2\ell+1)\cos^2\left(\mathbf{k}\cdot\mathbf{r}' + \ell\frac{\pi}{2}\right)\frac{x^{\ell+2}j_{\ell+1}(\alpha x)}{g_{\ell+1}(x)}\mathscr{I}_\ell^+(x,\alpha)$$
$$+ \frac{x}{1+x}\Delta^2 \sum_{\ell=0}^{\infty}(-1)^{\ell+1}(2\ell+1)\cos^2\left(\mathbf{k}\cdot\mathbf{r}' + \ell\frac{\pi}{2}\right)$$
$$\times\left\{\frac{1}{2}\frac{g_{\ell+1}(-x)}{g_{\ell+1}(x)}\left[\mathscr{I}_\ell^+(x,\alpha)\right]^2 + \mathscr{I}_\ell^+(x,\alpha)\mathscr{I}_\ell^-(x,\alpha) - \mathscr{I}_\ell^0(x,\alpha)\right\}\,. \tag{D.32}$$

References

[1] E.E. Salpeter, Ann. Phys. 5 (1958) 183.
[2] R. Abe, Progr. Theory Phys. 22 (1959) 213.
[3] M. Baus, J.-P. Hansen, Phys. Rep. 59 (1980) 1.
[4] S. Alexander, P.M. Chaikin, P. Grant, G.J. Morales, P. Pincus, D. Hone, J. Chem. Phys. 80 (1984) 5776.
[5] K. Kremer, M.O. Robbins, G.S. Grest, Phys. Rev. Lett. 57 (1986) 2694.
[6] Y. Levin, M.C. Barbosa, M.N. Tamashiro, Europhys. Lett. 41 (1998) 123.
[7] M.N. Tamashiro, Y. Levin, M.C. Barbosa, Physica A 258 (1998) 341.
[8] F.J. Rogers, H.E. DeWitt, (Eds.), Strongly Coupled Plasmas, Plenum Press, New York, 1987.
[9] G. Zerah, J. Clerouin, E.L. Pollock, Phys. Rev. Lett. 69 (1992) 446.
[10] K.-C. Ng, J. Chem. Phys. 61 (1974) 2680.
[11] Y. Rosenfeld, Phys. Rev. E 54 (1996) 2827.
[12] P. Debye, E. Hückel, Phys. Z. 24 (1923) 185, 305.
[13] D.A. McQuarrie, Statistical Mechanics, Harper-Collins, New York, 1976 (Chapter 15).
[14] S. Arrhenius, Z. Phys. Chem. 1 (1887) 631.
[15] S. Nordholm, Chem. Phys. Lett. 105 (1984) 302.
[16] R. Penfold, S. Nordholm, B. Jönsson, C. E. Woodward, J. Chem. Phys. 92 (1990) 1915.
[17] B.P. Lee, M.E. Fisher, Phys. Rev. Lett. 76 (1996) 2906.

[18] B.P. Lee, M.E. Fisher, Europhys. Lett. 39 (1997) 611.

[19] F.H. Stillinger, R. Lovett, J. Chem. Phys. 48 (1968) 3858.

[20] F.H. Stillinger, R. Lovett, J. Chem. Phys. 49 (1968) 1991.

[21] J.G. Kirkwood, Chem. Rev. 19 (1936) 275.

[22] [G. Stell, S.F. Sun, J. Chem. Phys. 63 (1975) 5333]

[23] [J.S. Høye, G. Stell, Mol. Phys. 52 (1984) 1071]

[24] M.E. Fisher, Y. Levin, Phys. Rev. Lett. 71 (1993) 3826.

[25] Y. Levin, X.-J. Li, M.E. Fisher, Phys. Rev. Lett. 73 (1994) 2716.

[26] Y. Levin, M.E. Fisher, Physica A 225 (1996) 164.

[27] H.E. DeWitt, Phys Rev. A 14 (1976) 1290.

[28] S. Galam, J.-P. Hansen, Phys. Rev. A 14 (1976) 816.

[29] A. Erdélyi, W. Magnus, F. Oberhettinger, F.G. Tricomi(Eds.), Higher Transcendental Functions, Bateman Manuscript Project, vol. II, McGraw-Hill, New York, 1953 (Chapter 7).

[30] M. Abramowitz, I.A. Stegun, (Eds.), Handbook of Mathematical Functions with Formulas, Graphs, and Mathematical Tables, National Bureau of Standards, Applied Mathematics Series, vol. 55 U.S. Government Printing Office, Washington D.C., 1964 (Chapter 10).

[31] J.D. Jackson, Classical Electrodynamics, second ed., sect. 3.9, Wiley, New York, 1975.