This too may be a reasonable approximation, at least for hard spheres. In Lozada-Cassou's scheme there are 5 missing integrals and 2 spurious integrals. As a result it is difficult to pair terms and simple minded arguments, such as that given above, are proba bly not informative.

8. Summary

Six approximation for g_{123} have been considered. The superposition approximation and Eq. (23) are too simple, the Lozada — Cassou and Attard approximations are more sophisticated but more difficult computationally. Equation (36) is even more demanding computationally. Equation (26) may be the best compromise between sophistication and ease of use.

All of the approximations which we have considered neglect $(\delta 3_{123})^2$. There is no difficulty in including this integral. Each approximation can be cast in a HNC version, rather than the PY version considered here, by considering $\ln g_{123}$ rather than g_{123}. Probably the PY version would be best for hard spheres but the HNC version might be preferable for other systems.

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INTEGRAL EQUATIONS FOR THE CORRELATION FUNCTIONS OF FLUIDS NEAR WALLS

An integral equations for the correlation functions of fluids near impenetrable wall are considered within the singlet and pair theory. The main attention is paid to the treatment of the long-range Coulomb interparticle and particle-wall interactions.

1. Introduction

Despite recent progress in the description of the electrode — electrolyte interface the theory of electric double layer is still not complete. Integral equations form a basis for studies in this area and a wide set of models within different approximate schemes has been investigated.

In this article we have two goals. First, we should like to present a brief but consistent general route of the integral equations application for the electrolyte/wall problem. On the other hand we shall introduce some important supplements which are helpful methodologically as well as necessary for the numerical treatment. The singlet theory which provides the density profiles of particles near the wall will be discussed first. Then, a natural development leads to the so-called pair theory which gives both the profiles and pair functions of inhomogeneous fluid.

2. General theory at the "Singlet" level

At the beginning it is necessary to discuss briefly the models which will be considered and their applicability. Most important is that this study is restricted to those systems in which the ions interact via isotropic short-ranged and long-ranged Coulomb electrostatic potentials. The ions possess neither a dipole moment nor higher order multipole moments. So, the primitive model of electrolyte solutions and the fused salts belong to this class.

As usual, this class of models can be described by a set of reduced dimensionless parameters, i. e. the packing fraction $\eta = \pi \sum_i \rho_i d_{ii}^3/6$, $\beta_i^* = q_i^2/kT\varepsilon d_{ii}$, size and charge ratios, where q_i and d_{ii} are the charge and diameter of the particles respectively. Due to difference in dielectric constant ε between the primitive model of an electrolyte solution and the fused salt case and corresponding temperature region, the strength of interactions (β_i^*) is very different. Although not especially important for an analytic treatment, it could cause severe problems in the numerical procedures. The particle-hard wall interactions are described by the single parameter $E^* = (kTd_{ii}^3)^{1/2}E$ where $E = 4\pi\sigma/\varepsilon$ is the electric field value on the wall and σ is the charge per unit area on the wall.

Now, proceeding we define the singlet theory, in contrast to the pair theory presented in the following sections. This classification has been introduced not so long ago by Henderson et al. [1, 2] and discussed in [3]. At the present, we merely state that the singlet theory is the one which does not utilize the inhomogeneous Ornstein — Zernike equation to calculate the density profiles and higher-order distribution functions of particles near a surface.

In fact, the inhomogeneity in the singlet theory is created by the presence of giant particles in the system which are at infinite dilution. This type of theory has been developed first by D. Henderson, F. F. Abraham, J. A. Barker [4] and J. K. Percus [5]. We shall start this presentation from the Ornstein — Zernike (OZ) equation for the correlation functions of a many-sort mixture. One of the species will be denoted by the index w and will be used in the following derivation to create a wall

$$h_{wi}(r_{12}) = c_{wi}(r_{12}) + \sum_l \rho_l \int dr_3 h_{wl}(r_{13})\, c_{li}(r_{32}). \qquad (2.1)$$

In order to create a wall one has to take two limits in (2.1), namely the infinite dilution of w particles and then increase to infinity their sizes. We shall assume the first limit provided and so the sum in (2.1) does not contain the w species. Rewrite now Eq. (2.1) in the bipolar coordinates to integrate by the third particle

$$h_{wi}(r_{12}) = c_{wi}(r_{12}) + \frac{2\pi}{r_{12}} \sum_l \rho_l \int_0^\infty dr_{13} r_{13} h_{wl}(r_{13}) \int_{|r_{12}-r_{13}|}^{r_{12}+r_{13}} dr_{32} r_{32} c_{li}(r_{32}). \qquad (2.2)$$

There is no distinction yet between $c_{wi}(r)$ and $c_{li}(r)$. At this point we shall restrict ourselves to the HNC closure for all direct correlation functions

$$c_{ij}^{(\mathrm{HNC})}(r) = -\beta\varphi_{ij}(r) - \beta q_i q_j/\varepsilon r + h_{ij}(r) - \ln[1 + h_{ij}(r)], \qquad (2.3)$$

where $\varphi_{ij}(r)$ is the short-range part of the total pair interaction. Then, Eq. (2.2) is

$$\ln[1 + h_{wi}(r_{12})] = -\beta\varphi_{wi}(r_{12}) - \beta q_i q_w/\varepsilon r_{12} + \frac{2\pi}{r_{12}} \sum_l \rho_l \int_0^\infty dr_{13} r_{13} h_{wl}(r_{13}) \int_{|r_{12}-r_{13}|}^{r_{12}+r_{13}} dr_{32} r_{32} c_{li}^*(r_{32}^*) - \frac{2\pi}{r_{12}} \frac{\beta q_i}{\varepsilon} \sum_l \rho_l q_l \int_0^\infty dr_{13} r_{13} h_{wl}(r_{13}) \int_{|r_{12}-r_{13}|}^{r_{12}+r_{13}} dr_{32}, \qquad (2.4)$$

where

$$c_{li}^{*}(r) = -\beta\varphi_{li}(r) + h_{li}(r) - \ln[1 + h_{li}(r)]. \tag{2.5}$$

Now, the last integral in (2.4) can be transformed as follows

$$-\frac{2\pi}{r_{12}}\frac{\beta q_i}{\varepsilon}\sum_l \rho_l q_l \int_0^\infty dr_{13} r_{13} h_{wl}(r_{13}) \int_{|r_{12}-r_{13}|}^{r_{12}+r_{13}} dr_{32} =$$

$$= -\frac{4\pi}{r_{12}}\frac{\beta q_i}{\varepsilon}\sum_l \rho_l q_l \int_0^\infty dr_{13} r_{13} h_{wl}(r_{13}) +$$

$$+ \frac{4\pi}{\varepsilon}\beta q_i \sum_l \rho_l q_l \int_{r_{12}}^\infty dr_{13} \frac{r_{13}(r_{13}-r_{12})}{r_{12}} h_{wl}(r_{13}). \tag{2.6}$$

Making use of the local electroneutrality condition

$$q_w = -4\pi \sum_l \rho_l q_l \int_0^\infty dr r^2 h_{wl}(r) \tag{2.7}$$

then Eq. (2.4) is

$$\ln[1 + h_{wi}(r_{12})] = -\beta\varphi_{wi}(r_{12}) + \frac{2\pi}{r_{12}}\sum_l \rho_l \int_0^\infty dr_{13} r_{13} h_{wl}(r_{13}) \times$$

$$\times \int_{|r_{12}-r_{13}|}^{r_{12}+r_{13}} dr_{32} r_{32} c_{li}(r_{32}) + \frac{4\pi}{\varepsilon}\beta q_i \sum_l \rho_l q_l \int_{r_{12}}^\infty dr_{13} \frac{r_{13}(r_{13}-r_{12})}{r_{12}} h_{wl}(r_{13}), \tag{2.8}$$

where the Coulomb terms have been combined. At this step in our derivation the wall is introduced. We write the variables r_{12} and r_{13} as $r_{12} = R + x$, $r_{13} = R + t$ and take the limit $R \to \infty$. Then, the Eq. (2.8) becomes

$$\ln[1 + h_{wi}(x)] = -\beta\varphi_{wi}(x) + 2\pi \sum_l \rho_l \int_{-\infty}^\infty dt h_{wl}(t) \times$$

$$\times \int_{|x-t|}^\infty dr r c_{li}^{*}(r) + \frac{4\pi}{\varepsilon}\beta q_i \sum_l \rho_l q_l \int_x^\infty dt (t - x) h_{wl}(t), \tag{2.9}$$

where the direct correlation function is given by (2.5).

3. Some electrostatic considerations

Let us define the mean electrostatic potential $\psi(x)$ as follows

$$\psi(x) = \frac{4\pi}{\varepsilon}\sum_l \rho_l q_l \int_x^\infty dt (x - t) h_{wl}(t). \tag{3.1}$$

Its derivatives are

$$\frac{d\psi(x)}{dx} = \frac{4\pi}{\varepsilon}\sum_l \rho_l q_l \int_x^\infty dt h_{wl}(t), \tag{3.2a}$$

$$\frac{d^2\psi(x)}{dx^2} = -\frac{4\pi}{\varepsilon}\sum_l \rho_l q_l h_{wl}(x) \tag{3.2b}$$

and therefore $\psi(x)$ satisfies Poisson's equation.

One can extract the total potential difference across the interface. We assume that the particle-wall interaction prevents penetration of particles into the wall, which is situated at $x = 0$, i. e.

$$\varphi(x) = \begin{cases} \infty, & x < 0, \\ \varphi(x), & x \geqslant 0. \end{cases} \tag{3.3}$$

Then, Eq. (2.9) is

$$\ln[1+h_i(x)] = -\beta\varphi_i(x) - \beta q_i\psi(x) + 2\pi\sum_l \rho_l \int_{-\infty}^{\infty} dth_l(t) \times$$

$$\times \int_{|x-t|}^{\infty} drrc_{li}^*(r) = -\beta\varphi_i(x) - \beta q_i\psi(0) - \frac{4\pi}{\varepsilon}\beta q_i \sum_l \rho_l q_l \left\{\int_0^{\infty} dtth_l(t) + \right.$$

$$\left. + x\int_x^{\infty} dth_l(t)\right\} + 2\pi\sum_l \rho_l \int_{-\infty}^{\infty} dth_l(t) \int_{|x-t|}^{\infty} drrc_{li}^*(r), \tag{3.4}$$

where the index w is omitted here and in the following for a simpler notation. Because the wall is impenetrable,

$$h_i(x) = -1, \quad x<0. \tag{3.5}$$

So the last term in (3.4), denoted $I_i(x)$, can be transformed as follows

$$I_i(x) = -2\pi\sum_l \rho_l \int_0^{\infty} dt \int_{x+t}^{\infty} drrc_{li}^*(r) + 2\pi\sum_l \rho_l \int_0^{\infty} dth_l(t) \int_{|x-t|}^{\infty} drrc_{li}^*(r) =$$

$$= -2\pi\sum_l \rho_l \int_x^{\infty} drrc_{li}^*(r) \int_0^{r-x} dt + 2\pi\sum_l \rho_l \int_0^{\infty} dth_l(t) \int_{|x-t|}^{\infty} drrc_{li}^*(r). \tag{3.6}$$

The moments of the short-ranged direct correlation functions $c_{ij}^*(r)$ will be introduced

$$f_{ij}^{(n)}(x) = \int_x^{\infty} drr^n c_{ij}^*(r). \tag{3.7}$$

With this notation the final form of Eq. (3.4) is

$$\ln[1+h_i(x)] = -\beta\varphi_i(x) - \beta q_i\psi(0) - 4\pi/\varepsilon(\beta q_i)\sum_l \rho_l q_l \left[\int_0^{x} dtth_l(t) + \right.$$

$$\left. + x\int_x^{\infty} dth_l(t)\right] + 2\pi\sum_l \rho_l \int_0^{\infty} dth_l(t) f_{li}^{(1)}(|x-t|) - 2\pi\sum_l \rho_l (f_{li}^{(2)}(x) - xf_{li}^{(1)}(x)). \tag{3.8}$$

We shall summarize the derivation at this point. Eq. (3.8) comprises HNC/HNC (wall/bulk) approximation for the model with an arbitrary short-range particle-wall interaction and long-range electrostatic Coulomb interaction. The bulk model also is flexible as for the short-range interaction. The model is to be solved in the HNC framework to provide the short-ranged part of direct correlation functions.

In accordance with Eq. (3.8) the contact value of the one-particle distribution function is given as

$$g_i(0) = \exp\left\{-\beta\varphi_i(0) - \beta q_i\psi(0) + 2\pi\sum_l \rho_l \int_0^{\infty} dth_l(t) f_{li}^{(1)}(t) - \right.$$

$$\left. - 2\pi\sum_l \rho_l f_{li}^{(2)}(0)\right\}. \tag{3.9}$$

One can check the data given by (3.9) if recalls the relation

$$\beta^{-1}\sum_i \rho_i g_i(0) = \frac{\varepsilon E^2}{8\pi} + \frac{1}{2}\left(\beta^{-1}\sum_i \rho_i - \chi^{-1}\right) \tag{3.10}$$

obtained by Carnie et al. [5], where χ is the compressibility of the bulk model, and where

$$E = -d\psi(x)/dx|_{x=0} = -4\pi/\varepsilon\sum_l \rho_l q_l \int_0^{\infty} dth_l(t). \tag{3.11}$$

If the particle-wall interaction contains a soft-core repulsive term and short-range attraction which give rise to a tail $\varphi_1(x)$ for the case of a simple fluid [6], then the contact value $g_i(x=0)$ is given by the relation similar to (3.10)

$$\beta^{-1}\Sigma\rho_i g_i(0) = \Sigma\rho_i \int_0^\infty dx g_i(x)\,\partial\varphi_i(x)/\partial x + \frac{1}{2}(\beta^{-1}\Sigma\rho_i + \chi^{-1}) + \frac{\varepsilon F^2}{8\rho}. \quad (3.12)$$

4. Pair theory for the correlation functions of inhomogeneous fluid

As we have already mentioned the singlet theory utilizes the homogeneous Ornstein — Zernike equation, i. e. the OZ equation which contains constant density. On the contrary to the singlet theory, the pair theory consists of the inhomogeneous OZ equation and additional equation which provides coupling between the profile and pair distribution function. There are three unknown functions $h_{ij}(r_1, r_2)$, $c_{ij}(r_1, r_2)$ and $\rho_i(r)$ in this problem. For the completeness, some kind of closure has to be applied. The closure comprises the relationship between the inhomogeneous pair correlation function $h_{ij}(r_1, r_2)$ and direct correlation function $c_{ij}(r_1, r_2)$, and besides that contains the interaction potential. Let us write down necessary equations. The first is the OZ equation for inhomogeneous system

$$h_{ij}(r_1, r_2) - c_{ij}(r_1, r_2) = \sum_l \int dr_3 \rho_l(r_3)\, h_{il}(r_1, r_3)\, c_{lj}(r_3, r_2). \quad (4.1)$$

It has to supplemented by additional equation for the profiles and pair functions. There are three equivalent possibilities to define this coupling, either in the form of Lovett — Mou — Buff — Wertheim (LMBW) equation [7, 8]

$$kT\nabla_1 \ln\rho_i(r_1) + \nabla_1 V_i^{(ext)}(r_1) + \sum_l \int dr_2 \rho_i(r_2)\, h_{il}(r_1, r_2)\, \nabla_2 V_l^{(ext)}(r_2) = 0 \quad (4.2)$$

or

$$\nabla_1 \ln\rho_i(r_1) = -(kT)^{-1}\nabla_1 V_i^{(ext)}(r_1) + \sum_l \int dr_2 c_{il}(r_1, r_2)\, \nabla_2 \rho_l(r_2) \quad (4.3)$$

or Born — Green equation

$$\nabla_1 \ln\rho_i(r_1) = -(kT)^{-1}\nabla_1 V_i^{(ext)}(r_1) - (kT)^{-1}\sum_l \int dr_2 \frac{\rho_{il}(r_1, r_2)}{\rho_i(r_1)} \nabla U_{il} \times (r_1 - r_2), \quad (4.4)$$

where $V_i^{(ext)}(r)$ is the external potential providing the inhomogeneity,

$$\rho_{ij}(r_1, r_2) = \rho_i(r_1)\rho_j(r_2)[1 + h_{ij}(r_1, r_2)] \quad (4.5)$$

is the inhomogeneous pair distribution function. The equation (4.3) is often called the Triezenberg — Zwanzig equation [9].

So, the problem formulated consist of (4.1), any of the equations (4.3) — (4.5) and the closure relation for inhomogeneous direct correlation function. Let us rewrite the pair of equations which comprises the problem for the case of planar geometry

$$h_{ij}(z_1, z_2, R_{12}) = c_{ij}(z_1, z_2, R_{12}) + \sum_l \int dz_3 \rho_l(z_3) \int dR_3 h_{il}(z_1, z_3, R_{13})\, c_{lj}(z_3, z_2, R_{32}), \quad (4.6)$$

$$\frac{\partial}{\partial z_1} \ln\rho_i(z_1) = -(kT)^{-1}\frac{\partial}{\partial z_1} V_i^{(ext)}(z_1) + \sum_l \int dz_2 \frac{\partial\rho_l(z_2)}{\partial z_2} \int dR_{12} c_{il}(z_1, z_2, R_{12}), \quad (4.7)$$

where all the integrations by R are two-dimensional. Now we shall recall that the pair interparticle interactions consist of short-ranged and Coulomb terms and the external potential is

$$V_i^{(ext)}(z) = \varphi_i(z) - q_i E z. \qquad (4.8)$$

5. Treatment of coulomb interactions

Our target in the following derivation is to combine long-range Coulomb terms in favour of the mean electrostatic potential. We shall deal first with inhomogeneous OZ equation and assume the following closure for the inhomogeneous direct correlation function

$$c_{ij}(1,2) = c_{ij}^{*}(1,2) - \beta q_i q_j/\varepsilon r_{12}, \qquad (5.1)$$

where $r_{12} = [(z_1 - z_2)^2 + R_{12}^2]^{1/2}$. Then the Eq. (4.6) is

$$h_{ij}(r_1, r_2) = c_{ij}^{*}(r_1, r_2) + 2\pi \sum_l \int_{-\infty}^{\infty} dz_3 \int_0^{\infty} dR_3 R_3 \rho_l(z_3) h_{il}(r_1, r_3) c_{lj}^{*}(r_3, r_2) -$$

$$- \beta q_i q_j/\varepsilon R_{12} - 2\pi q_j/\varepsilon \sum_l q_l \int_{-\infty}^{\infty} dz_3 \int_0^{\infty} dR_3 R_3 \rho_l(z_3) h_{il}(r_1, r_3) \frac{1}{R_{32}}. \qquad (5.2)$$

If the charge electroneutrality will be utilized

$$q_i = -2\pi \sum_l q_l \int_{-\infty}^{\infty} dz_3 \rho_l(z_3) \int_0^{\infty} dR_3 R_3 h_{il}(\boldsymbol{r}_1, \boldsymbol{r}_3) \qquad (5.3)$$

then Eq. (5.2) is

$$h_{ij}(r_1, \boldsymbol{r}_2) = c_{ij}^{*}(r_1, r_2) + 2\pi \sum_l \int_{-\infty}^{\infty} dz_3 \rho_l(z_3) \int_0^{\infty} dR_3 R_3 h_{il}(\boldsymbol{r}_1, \boldsymbol{r}_3) \times$$

$$\times c_{lj}^{*}(\boldsymbol{r}_3, \boldsymbol{r}_2) - \beta q_i \psi_i(\boldsymbol{r}_1, \boldsymbol{r}_2). \qquad (5.4)$$

We have introduced the function

$$\psi_i(\boldsymbol{r}_1, \boldsymbol{r}_2) = 2\pi/\varepsilon \sum_l q_l \int_{-\infty}^{\infty} dz_3 \rho_l(z_3) \int_0^{\infty} dR_3 R_3 h_{il}(\boldsymbol{r}_1, \boldsymbol{r}_3) \left[\frac{1}{R_{32}} - \frac{1}{R_{12}}\right]. \qquad (5.5)$$

Let us inspect the behaviour of $\psi_1(\boldsymbol{r}_1, \boldsymbol{r}_2)$ at distances z_1, z_2 far from the electrode. Actually we would like to look for a homogeneous analogue of $\psi_i(\boldsymbol{r}_1, \boldsymbol{r}_2)$. So, if one assumes $\rho_i(z_3) = \rho_i$ and $h_{il}(\boldsymbol{r}_1, \boldsymbol{r}_3) = h_{il}(R_{13})$, then (7.5) has the form

$$\psi_i(R_{12}) = \sum_l \rho_l q_l/\varepsilon \int d\boldsymbol{R}_3 h_{il}(R_{13}) [1/R_{32} - 1/R_{12}] =$$

$$= 2\pi/\varepsilon R_{12} \sum_l \rho_l q_l \int_0^{\infty} dR_{13} R_{13} h_{il}(R_{13}) \int_{|R_{12}-R_{13}|}^{R_{12}+R_{13}} dR_{32}(1 - R_{32}/R_{12}) =$$

$$= 4\pi/\varepsilon R_{12} \sum_l \rho_l q_l \int_{R_{12}}^{\infty} dR_{13} R_{13}(R_{12} - R_{13}) h_{il}(R_{13}). \qquad (5.6)$$

Now, if one compare this expression with the last term of (2.8) and (3.1), it becomes clear that $\psi_i(\boldsymbol{r}_1, \boldsymbol{r}_2)$ could be treated as a species dependent pair mean electrostatic potential. It is evident that $\psi_i(\boldsymbol{r}_1, \boldsymbol{r}_2)$ is a more short-ranged function than the input interactions. However, the detailed study of $\psi_1(\boldsymbol{r}_1, \boldsymbol{r}_2)$ behaviour in the wall plane is desirable.

Let us consider now the treatment of Coulomb interactions in the LMBW equation. Substitution of (5.1) into (4.7) leads to the equation

$$\frac{\partial \ln \rho_i(z_1)}{\partial z_1} + \beta \frac{\partial \varphi_i(z_1)}{\partial z_1} - \frac{\partial}{\partial z_1}(\beta q_1 E z_1) = 2\pi \sum_l \rho_l \int_{-\infty}^{\infty} dz_2 \partial g_l(z_2)/\partial z_2 \times$$

$$\times \int_0^{\infty} dR R c_{il}^{*}(z_1, z_2, R) - 2\pi\beta q_i/\varepsilon \sum_l \rho_l q_l \int_{-\infty}^{\infty} dz_2 \partial g_1(z_2)/\partial z_2 \int_{|z_1-z_2|}^{\infty} dR, \qquad (5.7)$$

where $\rho_i(z) = \rho g_i(z)$. The wall is impenetrable at $z < 0$, hence the profiles $g_i(z)$ has the form $g_i(z) H(z)$, where $H(z)$ is the step function. After transformation of the last integral in (5.7) at $z_2 < 0$, we obtain from (5.7)

$$\frac{\partial \ln \rho_i(z_1)}{\partial z_1} + \beta \frac{\partial \varphi_i(z_1)}{\partial z_1} - \beta q_i E = 2\pi \sum_l \rho_l \int_{-\infty}^{\infty} dz_2 \frac{\partial g_l(z_2)}{\partial z_2} \times$$

$$\times \int_0^{\infty} dRRc^*_{il}(z_1, z_2, R) - \frac{2\pi\beta q_i}{\varepsilon} \sum_l \rho_l q_l g_l(0) \int_{z_1}^{\infty} dR -$$

$$- \frac{2\pi\beta q_i}{\varepsilon} \sum_l \rho_l q_l \int_0^{\infty} dz_2 \frac{\partial g_l(z_2)}{\partial z_2} \int_{|z_1-z_2|}^{\infty} dR. \tag{5.8}$$

Let us transform further the last integral in (5.8). Since $\partial g_l(z_2)/\partial z_2 = \partial h_l(z_2)/\partial z_2$ at $z_2 > 0$ ($h_l(z_2) = g_l(z_2) - 1$), then integrating by parts one obtains

$$- \frac{2\pi\beta q_i}{\varepsilon} \sum_l \rho_l q_l \int_0^{\infty} dz_2 \frac{\partial h_l(z_2)}{\partial z_2} \int_{|z_1-z_2|}^{\infty} dR =$$

$$= - \frac{2\pi\beta q_i}{\varepsilon} \sum_l \rho_l q_l \left\{ \left[h_l(z_2) \int_{|z_1-z_2|}^{\infty} dR \right] \Big|_0^{\infty} + \int_0^{\infty} dz_2 h_l(z_2)\, \partial/\partial z_1 \int_{|z_2-z_1|}^{\infty} dR \right\} =$$

$$= - \frac{2\pi\beta q_i}{\varepsilon} \sum_l \rho_l q_l \left\{ - g_l(0) \int_{z_1}^{\infty} dR + \int_0^{\infty} dz_2 h_l(z_2)\, \partial/\partial z_1 \int_{|z_1-z_2|}^{\infty} dR \right\}. \tag{5.9}$$

In (5.9) we have utilized the electroneutrality condition $\Sigma \rho_l q_l = 0$ and $\partial/\partial z_2 = -\partial/\partial z_1$.

Substituting (5.9) into (5.8), the latter is

$$\frac{\partial \ln \rho_i(z_1)}{\partial z_1} + \beta \frac{\partial \varphi_i(z_1)}{\partial z_1} = 2\pi \sum_l \rho_l \int_{-\infty}^{\infty} dz_2 \frac{\partial g_l(z_2)}{\partial z_2} \int_0^{\infty} dRRc^*_{il}(z_1, z_2, R) -$$

$$- \beta q_i \frac{\partial}{\partial z_1} \Psi(z_1), \tag{5.10}$$

where

$$\Psi(z_1) = - Ez_1 + \frac{2\pi}{\varepsilon} \sum_l \rho_l q_l \int_0^{\infty} dz_2 h_l(z_2) \int_{|z_1-z_2|}^{\infty} dR \tag{5.11}$$

can be treated as the mean electrostatic potential (see the Appendix).

Appendix

Consider the treatment of Coulomb terms for the case of planar geometry in the singlet theory. The HNC equation is

$$\ln[1 + h_i(z)] = - \beta V_i^{(\text{ext})}(z) + 2\pi \sum_l \rho_l \int_{-\infty}^{\infty} dt h_l(t) \int_{|z-t|}^{\infty} drrc_{il}(r), \tag{A.1}$$

with $V_i^{(\text{ext})}(z)$ given by (4.8) and $c_{il}(r)$ by (5.1). Then, (A.1) is

$$\ln[1 + h_i(z)] = - \beta\varphi_i(z) + \beta q_i Ez + 2\pi \sum_l \rho_l \int_{-\infty}^{\infty} dt h_l(t) \int_{|z-t|}^{\infty} drrc^*_{il}(r) -$$

$$- 2\pi\beta q_i/\varepsilon \sum_l \rho_l q_l \int_{-\infty}^{\infty} dt h_l(t) \lim_{l\to\infty} [L - |z-t|]. \tag{A.2}$$

Let us define the function

$$\Psi(z) = 2\pi/\varepsilon \sum_l \rho_l q_l \lim_{L\to\infty} L \int_{-\infty}^{\infty} dt h_l(t) - 2\pi/\varepsilon \Sigma \rho_l q_l \int_{-\infty}^{\infty} dt(|z-t|) h_l(t) -$$

$$- Ez + C', \tag{A.3}$$

where C' is an arbitrary constant because the mean electrostatic potential has arbitrary zero. The term proportional to L can be absorbed into the constant C' and (A.3) looks then as follows

$$\Psi(z) = -2\pi/\varepsilon \sum_l \rho_l q_l \int_{-\infty}^{\infty} dt\,(|z-t|)\,h_l(t) + 4\pi z/\varepsilon \sum_l \rho_l q_l \int_0^{\infty} dt h_l(t) + C, \tag{A.4}$$

where C denotes arbitrary constant. Since

$$\sum_l \rho_l q_l \int_{\infty-}^{0} dt h_l(t) = 0$$

then

$$\Psi(z) = -2\pi/\varepsilon \sum_l \rho_l q_l \int_{-\infty}^{0} dt h_l(t)\,(|z-t| - 2z) + C. \tag{A.5}$$

At large z $(z \to \infty)$

$$\Psi(z) = 2\pi/\varepsilon \sum_l \rho_l q_l \int_{-\infty}^{\infty} dt h_l(t)(z+t) + C. \tag{A.6}$$

Thus, the constant C can be determined

$$C = -2\pi/\varepsilon \sum_l \rho_l q_l \int_{-\infty}^{\infty} dt\,(z+t)\,h_l(t). \tag{A.7}$$

Now, substituting (A.7) into (A.5) one obtains

$$\Psi(z) = -4\pi/\varepsilon \sum_l \rho_l q_l \int_x^{\infty} dt h_l(t)\,(t-z), \tag{A.8}$$

which is the mean electrostatic potential and coincides with (3.1).

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