

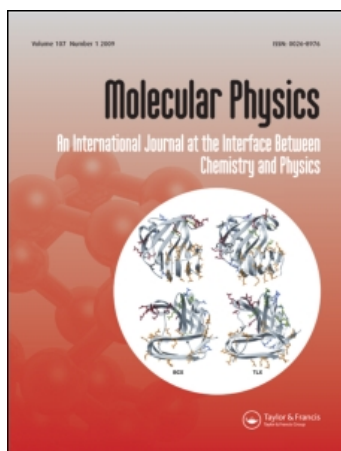
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### Charged hard spheres in a uniform neutralizing background using 'mixed' integral equations

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## Charged hard spheres in a uniform neutralizing background using 'mixed' integral equations

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The structure and thermodynamic properties of a collection of charged hard spheres immersed in a uniform neutralizing background are studied using 'mixed' integral equations, wherein the Percus-Yevick approximation is used with the hard-sphere part of the potential and the hypernetted-chain approximation for the correction due to the Coulomb tail. Numerical solutions are presented along a particular isotherm and a comparison is made with the results of the Mean Spherical Model for the same system.

### 1. INTRODUCTION

The non-linear integral equation approach to fluid state theory has become, with the help of the computer, a practical and often highly successful one. While there is no known integral equation for the pair distribution function  $g(r)$  which is suitable under all circumstances, there are today a number of approximate equations, each of which may be well matched with a particular type of intermolecular potential and conditions of temperature and density. Thus, for example, the extreme cases of a hard-core potential and a Coulomb potential can be reasonably well studied using respectively the Percus-Yevick [1] (PY) and hypernetted-chain [2] (HNC) integral equations [3, 4]. Neither of these equations, however, would be entirely suitable for these two potentials in combination, i.e. for charged hard spheres. For such a case, one might seek to construct another approximate equation better adapted to this potential [5]. But, as shown in recent publications [6, 7], the inverse procedure is also possible. One may instead adapt rather the potential itself to suit the strong points of known equations. Thus, for the case mentioned, the PY approximation could be used to study the effect of the hard core and the HNC approximation for the influence of the Coulomb potential. The results of such a 'mixed' approach are presented in this paper.

We consider a system of  $N$  hard spheres of diameter  $d$ , each carrying a charge  $Q$ , embedded in a uniform neutralizing background which for simplicity is allowed to permeate the spheres [8]. For a given configuration of the ions in the volume  $V$  the potential energy of the system is

$$U(\mathbf{r}^N) = \sum_{i < j} \phi(r_{ij}) - \frac{1}{2} \rho N \int d\mathbf{r} \frac{Q^2}{r}, \quad (1)$$

where  $\rho \equiv N/V$  and

$$\left. \begin{aligned} \phi(r) &= \infty, & r < d, \\ &= Q^2/r, & r > d. \end{aligned} \right\} \quad (2)$$

The pair distribution function (PDF) for the potential (2) is then obtained in two stages. First we find the PDF  $g_0(r)$  for just the hard-core potential

$$\left. \begin{aligned} \phi_0(r) &= \infty, & r < d \\ &= 0, & r > d \end{aligned} \right\} \quad (3)$$

using the PY equation (or actually any other suitable method). The complete PDF is then written

$$g(r) = g_0(r) + \Delta G(r), \quad (4)$$

where  $\Delta G$ , the correction due to the long-range Coulomb potential, is the solution of the equations [6]

$$\Delta C(r) = \Delta G(r) - \ln [g(r) \exp [\beta \phi_1(r)] / g_0(r)], \quad (5 a)$$

$$\Delta \tilde{G}(k) = \frac{[1 + \rho \tilde{G}_0(k)]^2 \Delta \tilde{C}(k)}{1 - \rho [1 + \rho \tilde{G}_0(k)] \Delta \tilde{C}(k)}, \quad (5 b)$$

which constitute the analogue of the HNC approximation when applied to just the correction  $\Delta G$  rather than to the complete pair distribution function. (Were the ideal gas, with  $g_0 = 1$ , used as the reference system in these equations, they would reduce to the usual HNC equations.) In equation (5 a),  $\phi_1(r)$  is the Coulomb potential for separations greater than the hard-sphere diameter and is undefined for smaller separations. Furthermore, we have put  $G_0(r) \equiv g_0(r) - 1$  in these expressions and have used a tilde to denote a Fourier transform; as usual,  $\beta \equiv (k_B T)^{-1}$ .

Equations (5) are to be solved iteratively. As with the HNC equation itself, it is preferable to obtain the unknown  $\Delta G(r)$  in the form

$$H(r) = \beta \phi_1(r) + \ln [g(r) / g_0(r)], \quad (6)$$

for which equations (5) become

$$\Delta C(r) = g_0(r) \{ \exp [H(r) - \beta \phi_1(r)] - 1 \} - H(r), \quad (7 a)$$

$$\tilde{H}(k) = \frac{[1 + \rho \tilde{G}_0(k)]^2 \Delta \tilde{C}(k)}{1 - \rho [1 + \rho \tilde{G}_0(k)] \Delta \tilde{C}(k)} - \Delta \tilde{C}(k). \quad (7 b)$$

The PDF is then finally obtained as

$$g(r) = g_0(r) \exp [H(r) - \beta \phi_1(r)]. \quad (8)$$

It is worth noting here that equations (7), when viewed as a perturbation scheme to incorporate the effects of a *weak* potential  $\phi_1(r)$  on the pair distribution function, may be approximately solved in a simple fashion. If  $\phi_1(r)$  possesses a Fourier transform, we may begin the iterations by assuming  $g^{(0)}(r) = g_0(r)$  or equivalently  $H^{(0)}(r) = \beta \phi_1(r)$ ; here the superscript labels the iteration. Then equations (7) give

$$\Delta C^{(0)}(r) = -\beta \phi_1(r) \quad (9 a)$$

$$\tilde{H}^{(1)}(r) = -\frac{[1 + \rho \tilde{G}_0(k)]^2 \beta \tilde{\phi}_1(k)}{1 + \rho [1 + \rho \tilde{G}_0(k)] \beta \tilde{\phi}_1(k)} + \beta \tilde{\phi}_1(k), \quad (9 b)$$

so that from (8) the corrected PDF after one iteration is

$$g^{(1)}(r) = g_0(r) \exp [-h(r)], \tag{10}$$

where

$$h(k) = \frac{[1 + \rho \tilde{G}_0(k)]^2 \beta \tilde{\phi}_1(k)}{1 + \rho [1 + \rho \tilde{G}_0(k)] \beta \tilde{\phi}_1(k)}. \tag{11}$$

Equations (10) and (11) constitute a simple, non-iterative approximation proposed earlier [9], as well as by Anderson and Chandler [10], who called it the exponential approximation.

In general, if the perturbing potential  $\phi_1(r)$  is not in some sense 'weak', as will be the case here, equations (7) may be readily solved numerically by continuing the iterations until self-consistency is reached. This is further discussed in § 2. For the specific potential at hand, once a solution  $g(r)$  is found we may compute the values of the internal energy  $E$ , the pressure  $p$ , and the Helmholtz free energy  $A$  from [6]

$$\frac{E}{NkT} - \frac{3}{2} = \frac{1}{2} \rho \int d\mathbf{r} [g(r) - 1] \frac{\beta Q^2}{r}, \tag{12}$$

$$\frac{pV}{NkT} - 1 = \frac{2}{3} \pi \rho d^3 g(d) + \frac{1}{6} \rho \int d\mathbf{r} [g(r) - 1] \frac{\beta Q^2}{r}, \tag{13}$$

$$\begin{aligned} \frac{A}{NkT} = \frac{A_0}{NkT} - \frac{1}{2} \rho \int d\mathbf{r} \left\{ \frac{1}{2} \Delta G(r)^2 + \Delta G(r) \right. \\ \left. - g(r) \ln \left[ \frac{g(r)}{g_0(r)} \right] - [g(r) - 1] \frac{\beta Q^2}{r} \right\} \\ + \frac{1}{2\rho(2\pi)^3} \int d\mathbf{k} \left\{ \frac{\rho \Delta \tilde{G}(k)}{1 + \rho \tilde{G}_0(k)} - \ln \left[ 1 + \frac{\rho \Delta \tilde{G}(k)}{1 + \rho \tilde{G}_0(k)} \right] \right\}. \tag{14} \end{aligned}$$

Here,  $A_0$  is the excess free energy due to the hard-sphere potential alone, for which we will take the PY result [11]. The appearance of  $g(r) - 1$  rather than  $g(r)$  alone when multiplying  $\beta Q^2/r$  in these expressions is a consequence of the uniform background which neutralizes the system.

Before terminating this section, we note that, in addition to equations (5), other approximate methods for incorporating the effects of a perturbing potential  $\phi_1(r)$  on a reference system with potential  $\phi_0(r)$  are easily obtained. Actually, equation (5 b) is exact and follows from the Ornstein-Zernike equations for the reference and perturbed systems [6]. The approximation is in equation (5 a), the exact version of which reads [6]

$$\begin{aligned} \Delta C(r) = \Delta G(r) - g_0(r) \exp [\beta \phi_0(r)] [g(r) \exp [\beta \phi_1(r)] / g_0(r) - 1] \\ + \Delta P(r) + \Delta B(r), \tag{15} \end{aligned}$$

where

$$\begin{aligned} \Delta P(r) = g_0(r) \exp [\beta \phi_0(r)] [g(r) \exp [\beta \phi_1(r)] / g_0(r) - 1] \\ - \ln [g(r) \exp [\beta \phi_1(r)] / g_0(r)]. \tag{16} \end{aligned}$$

Neglect of  $\Delta B$ , analogous to the HNC approximation, leads to equation (5 a). Alternatively, one could obtain a PY-type approximation [9] by assuming

$$\Delta B(r) \approx -\Delta P(r). \quad (17)$$

Both of these approximations are included in the more general expression

$$\Delta B(r) \approx m\Delta P(r), \quad (18)$$

where furthermore the parameter  $m$  could now be chosen to satisfy some imposed constraint, such as consistency between the pressures obtained from the virial and compressibility equations [12]. Other approximations are of course possible; the appropriateness of any particular one will evidently depend on the nature of the perturbing potential  $\phi_1(r)$ . In the remainder of this paper we shall study only the HNC-type approximation, equations (5), which seems well suited for the Coulomb potential [4]. It has in addition the advantage of permitting the direct evaluation of the free energy, equation (14).

## 2. NUMERICAL SOLUTIONS

For very large separations the functions  $H(r)$  and  $\Delta C(r)$  have the asymptotic forms

$$\left. \begin{aligned} H(r) &\sim \beta\phi_1(r), \\ \Delta C(r) &\sim -\beta\phi_1(r). \end{aligned} \right\} \quad (19)$$

Since here  $\phi_1(r)$  is the slowly vanishing Coulomb potential, serious truncation errors can arise when these functions are numerically integrated over a finite range. This troublesome feature of the Coulomb potential has motivated alternative versions of the PY and HNC equations based on infinite re-summations of their diagram expansions, which have the final effect of replacing the Coulomb potential with a shielded Coulomb potential [13, 14]. However, since the difficulty is merely numerical, rather than one of principle, it can be circumvented by appropriate numerical techniques. Here we follow the method of Springer *et al.* [4] in subtracting out the known long-range behaviour of  $H$  and  $\Delta C$ , working instead with the short-range functions

$$\left. \begin{aligned} H_s(r) &= H(r) - H_L(r), \\ \Delta C_s(r) &= \Delta C(r) + H_L(r), \end{aligned} \right\} \quad (20)$$

where

$$H_L(r) \equiv [1 - \exp(-\alpha r)]\beta Q^2/r \quad (21)$$

and  $\alpha$  is a disposable parameter chosen so as to make the function  $\psi_s(r)$ , defined below, negligibly small at the termination of the finite range of  $r$ . The version of equations (7) that is actually solved numerically, namely

$$\Delta C_s(r) = g_0(r)\{\exp[H_s(r) - \psi_s(r)] - 1\} - H_s(r), \quad (22 a)$$

$$\tilde{H}_s(k) = \frac{[1 + \rho\tilde{G}_0(k)]^2[\Delta\tilde{C}_s(k) - \tilde{H}_L(k)]}{1 - \rho[1 + \rho\tilde{G}_0(k)][\Delta\tilde{C}_s(k) - \tilde{H}_L(k)]} - \Delta\tilde{C}_s(k), \quad (22 b)$$

where

$$\psi_S(r) \equiv \exp(-\alpha r) \beta Q^2 / r, \quad (23)$$

$$\tilde{H}_L(k) = \frac{4\pi\beta Q^2 \alpha^2}{k^2(k^2 + \alpha^2)}, \quad (24)$$

now involves only short-range functions that can be numerically handled in the usual way.

The external parameters of this calculation are the ion density  $\rho$  and the temperature  $T$ . It is convenient to use the ion sphere radius  $a$ , where

$$\frac{4}{3}\pi a^3 \rho = 1, \quad (25)$$

as the unit of distance and the electrostatic energy at separation  $a$  as the unit of energy, with the usual parameter

$$\Gamma \equiv \beta Q^2 / a \quad (26)$$

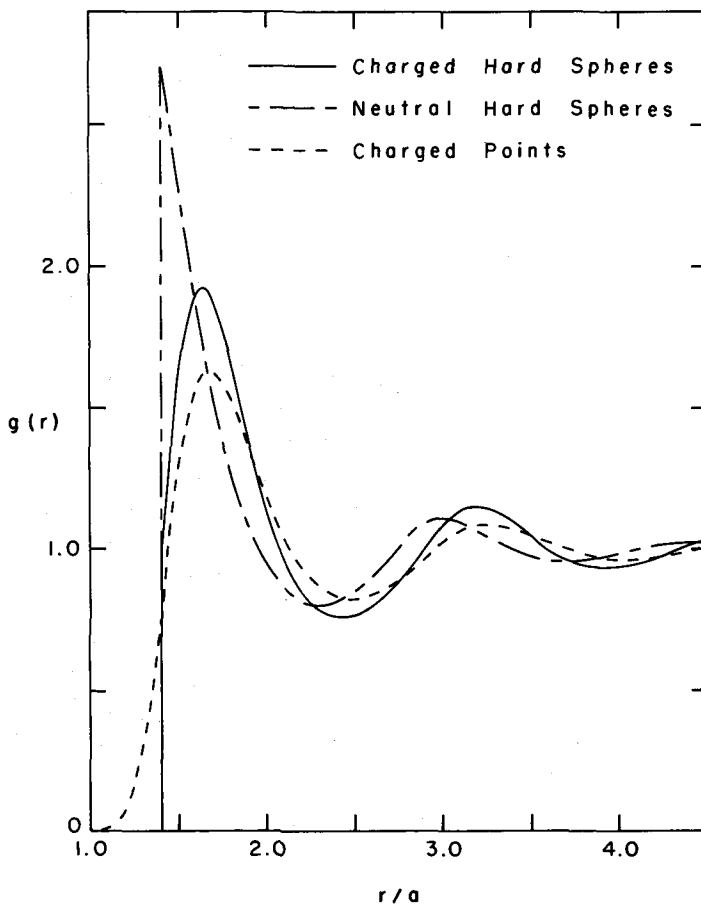


Figure 1. Pair distribution function for charged hard spheres at  $\Gamma=70$  with  $\Gamma_0=50$  (corresponding to a reduced hard sphere density of  $\rho d^3=0.6551$ ). Also shown for comparison are the  $g$ 's for neutral hard spheres at the same density and charged points at the same  $\Gamma$ .

incorporating both temperature and density specification. The other parameter which must be specified is now the reduced ion diameter

$$\sigma \equiv d/a. \quad (27)$$

More conveniently, solutions along a particular isotherm can be obtained by fixing

$$\Gamma_0 \equiv \beta Q^2/d, \quad (28)$$

so that  $\sigma = \Gamma/\Gamma_0$  and  $\Gamma$  is the only input parameter remaining to be specified.

Chihara [5] has applied a new integral equation to a similar model system, obtaining solutions for  $g(r)$  corresponding to the choices  $Q=e$ , the electronic charge,  $d=3.4 \text{ \AA}$ , and  $T=500^\circ\text{C}$ , which lead to the value  $\Gamma_0=63.57$ . In his solutions, however, a modified form of the Coulomb potential is used, so that direct comparisons cannot be made with the results below. For reasons of numerical convenience, we have chosen  $\Gamma_0=50$ , which, with the same values of  $Q$  and  $d$  as above, corresponds to a temperature of  $709.8^\circ\text{C}$ .

Equations (22) have been solved for the cases  $\Gamma=2.5, 5.0, 10(10)80$  and, as

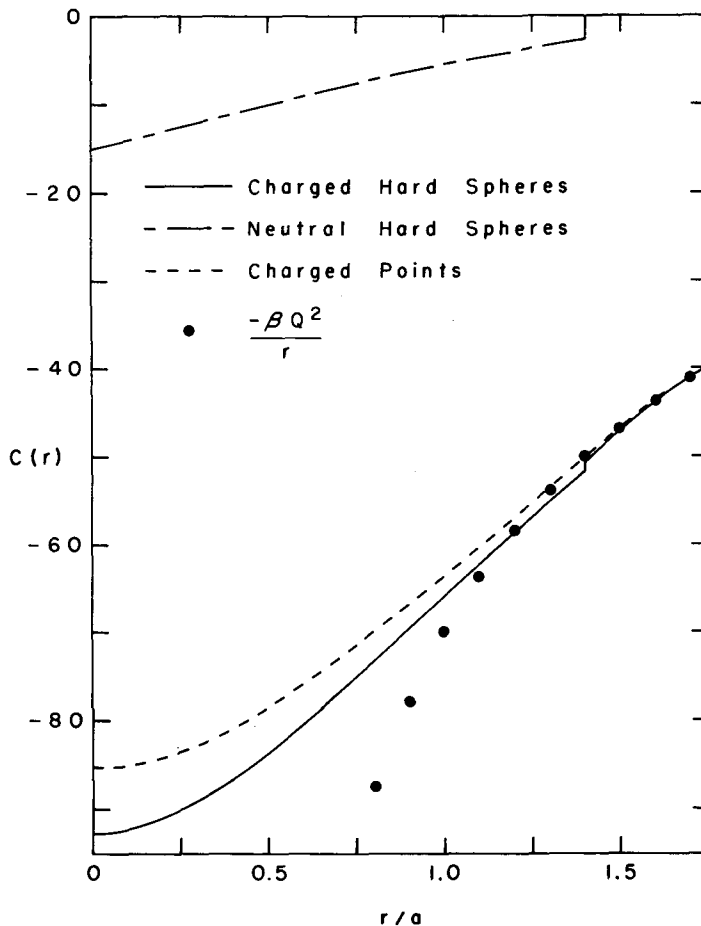


Figure 2. Direct correlation function for the same cases shown in figure 1.

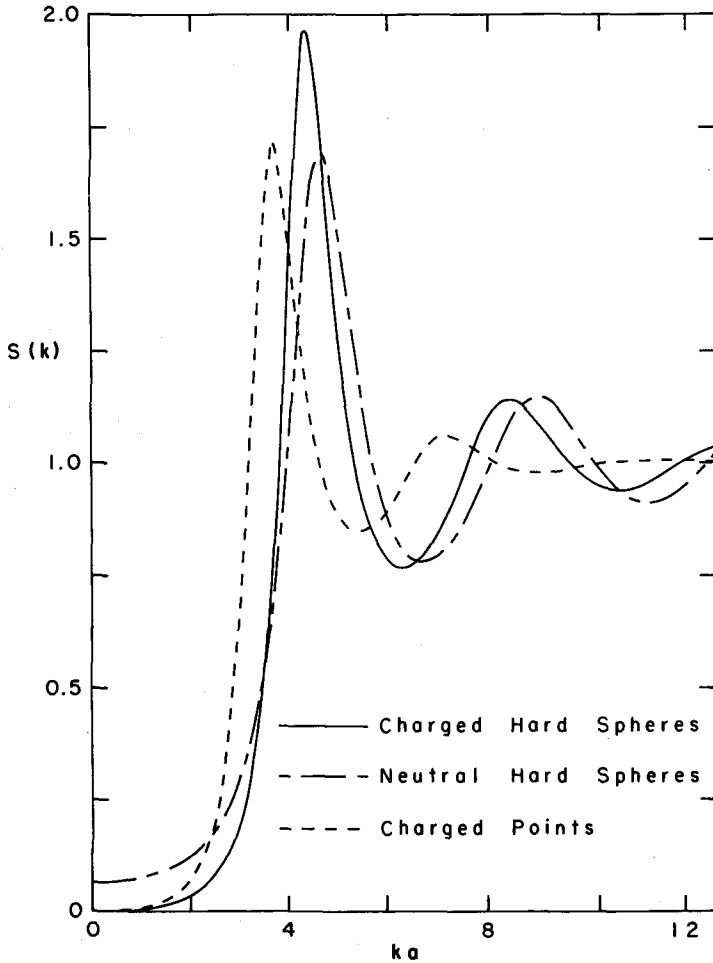


Figure 3. Structure factor  $S(k) = 1 + \rho \tilde{G}(k)$  for the same cases shown in figure 1.

$\Gamma$	$\rho d^3$	$\frac{E}{NkT} - \frac{3}{2}$	$\frac{pV}{NkT} - 1$	$\frac{A - A_{ideal}}{NkT}$
2.5	0.00003	-1.706	-0.5685	-1.391
5.0	0.0002	-3.732	-1.244	-3.190
10	0.0019	-7.936	-2.645	-7.060
20	0.0153	-16.54	-5.513	-15.19
30	0.0516	-25.24	-8.415	-23.54
40	0.1222	-34.00	-11.33	-32.00
50	0.2387	-42.79	-14.26	-40.54
60	0.4125	-51.68	-17.11	-49.20
70	0.6551	-60.92	-18.90	-57.90
80	0.9778	-70.70	-14.96	-65.67

Table 1. Computed thermodynamic parameters of charged hard spheres in a neutralizing background, using 'mixed' PY and HNC integral equations, along an isotherm defined by  $\beta Q^2/d = 50$ . The second column shows the corresponding reduced hard-sphere density.



noted,  $\Gamma_0 = 50$ . The choice of interval for the discrete numerical transforms [15] was in all cases  $\Delta r/a = 0.025$  and the range of integration went from  $r/a = 7.5$  for  $\Gamma = 2.5$  to  $r/a = 22.5$  for  $\Gamma = 80$ ; iterations were started with the initial guess  $H_S^{(0)}(r) = 0$  and were continued until the largest difference between successive iterates of  $rH_S(r)$  was smaller than  $10^{-4}$ . In all cases the PY solution [11] was used for the hard sphere  $g_0(r)$ .

The computed values of internal energy, pressure, and free energy are shown in table 1†. For the most part, these results are scarcely distinguishable from those of a pure Coulomb potential [4, 16], a fact largely explained by the low densities of the hard spheres that follow from most of the  $\Gamma$  values, as shown in table 1. At higher densities, the quantity most sensitive to the finite size of the ions is the pressure.

The pair distribution functions, tabulated in table 2, show more variability. At low  $\Gamma$  values, the computed  $g(r)$  are, as expected, practically the same as

(a)

$r/a$	$\Gamma$				
	2.5	5.0	10	20	30
0.5	0.082	0.009	0.000	0.000	0.000
0.6	0.175	0.039	0.002	0.000	0.000
0.7	0.294	0.109	0.015	0.000	0.000
0.8	0.421	0.220	0.061	0.005	0.000
0.9	0.544	0.362	0.161	0.031	0.006
1.0	0.654	0.514	0.317	0.116	0.041
1.1	0.747	0.658	0.508	0.289	0.159
1.2	0.821	0.781	0.700	0.535	0.394
1.3	0.878	0.876	0.864	0.798	0.708
1.4	0.920	0.945	0.985	1.017	1.011
1.5	0.950	0.990	1.061	1.160	1.224
1.6	0.971	1.015	1.097	1.225	1.324
1.7	0.984	1.028	1.105	1.229	1.330
1.8	0.993	1.031	1.095	1.196	1.277
1.9	0.998	1.029	1.075	1.145	1.198
2.0	1.001	1.024	1.053	1.090	1.116
2.2	1.003	1.013	1.015	1.002	0.986
2.4	1.003	1.004	0.993	0.959	0.926
2.6	1.002	1.000	0.987	0.956	0.926
2.8	1.001	0.999	0.990	0.975	0.962
3.0	1.000	0.999	0.996	0.996	1.001
3.2	1.000	0.999	1.000	1.009	1.023
3.4	1.000	1.000	1.002	1.011	1.024
3.6	1.000	1.000	1.002	1.007	1.012
4.0	1.000	1.000	1.000	0.998	0.993

† As noted by Springer *et al.* [4] computed thermodynamic values involving the Coulomb potential are more stable with respect to variation in the range of the computed  $g(r)$  when evaluated using Fourier transforms rather than direct space functions. Thus, the direct space integrals in equations (12)–(14) were first converted to equivalent transform space integrals; these were then numerically evaluated to obtain the values tabulated in table 1. Also, the excess free energy of hard spheres alone, which enters the total free energy in table 1, was calculated using the PY *virial* equation of state.

(b)

$r/a$	$\Gamma$				
	40	50	60	70	80
1.1	0.085	0.044	0.000	0.000	0.000
1.2	0.283	0.198	0.134	0.000	0.000
1.3	0.615	0.525	0.441	0.000	0.000
1.4	0.983	0.944	0.907	1.027	0.000
1.5	1.266	1.295	1.337	1.613	0.000
1.6	1.405	1.477	1.569	1.907	4.203
1.7	1.416	1.494	1.589	1.868	3.610
1.8	1.346	1.408	1.475	1.637	2.599
1.9	1.242	1.280	1.312	1.362	1.678
2.0	1.135	1.150	1.154	1.125	1.040
2.2	0.972	0.957	0.932	0.840	0.500
2.4	0.897	0.871	0.841	0.757	0.488
2.6	0.899	0.876	0.851	0.799	0.673
2.8	0.950	0.939	0.931	0.925	0.916
3.0	1.007	1.014	1.027	1.082	1.163
3.2	1.038	1.054	1.075	1.148	1.399
3.4	1.036	1.049	1.062	1.089	1.294
3.6	1.017	1.020	1.020	0.998	0.900
3.8	0.997	0.992	0.984	0.945	0.736
4.0	0.986	0.979	0.965	0.938	0.798
4.4	0.994	0.992	0.993	1.006	1.087
4.8	1.005	1.009	1.015	1.033	1.127
5.2	1.002	1.003	1.002	0.991	0.896
5.6	0.998	0.996	0.993	0.985	0.949
6.0	0.999	0.999	0.999	1.007	1.079

Table 2. Computed values of the pair distribution function of charged hard spheres in a neutralizing background, using 'mixed' PY and HNC integral equations, along an isotherm defined by  $\beta Q^2/d = 50$ .

those of the pure Coulomb potential [4]. For  $\Gamma = 80$ , however,  $g(r)$  for the combined potentials is close to the hard sphere PDF, except in the vicinity of the main peak where it is by comparison depressed as a consequence of the additional repulsion.

The case  $\Gamma = 70$ , which results in  $\sigma = 1.4$  and  $\rho d^3 = 0.6551$ , leads to the  $g(r)$  which is most distinct, among the solutions presented, from both the pure hard sphere and pure Coulomb limits. This function is shown in figure 1, along with the corresponding hard sphere and Coulomb solutions obtained from the PY and HNC equations, respectively. There is an evident overall increase in structure in comparison with the Coulomb case; compared to neutral hard spheres, the extra repulsion of the charged hard spheres results in a depression of the main peak and a shift of the overall curve away from the origin.

The corresponding shapes of the direct correlation function  $C(r)$  for the same solutions are shown in figure 2. One sees that the difference between  $C(r)$  for charged points and charged hard spheres is significant only within the hard-sphere diameter  $\sigma = 1.4$  and slightly beyond, both curves soon merging into the limiting shape of  $-\beta Q^2/r$ . The direct correlation function for the charged spheres is in addition discontinuous at the hard-sphere diameter.

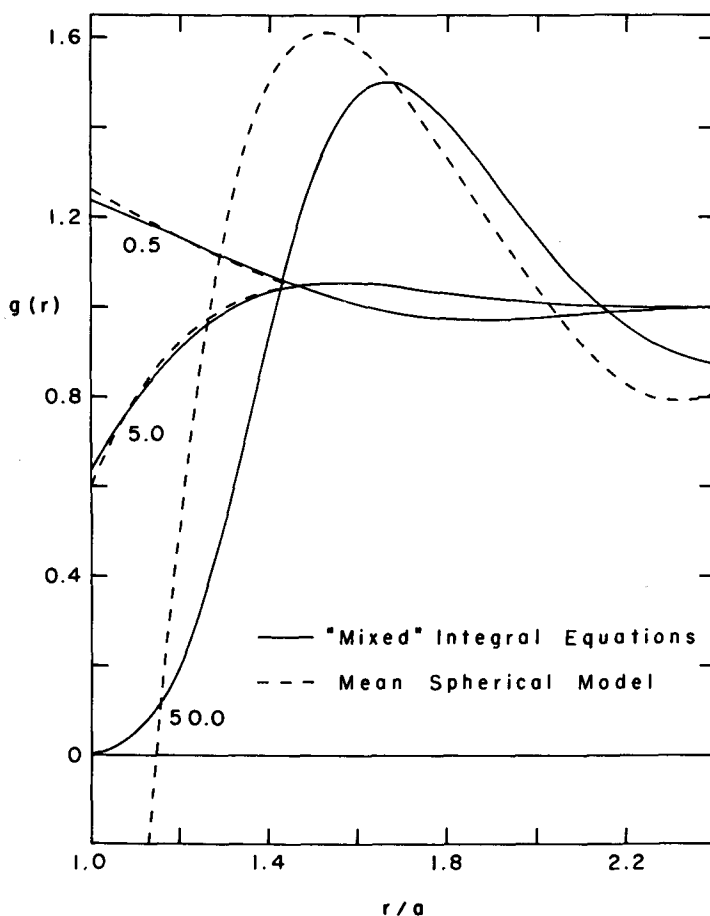


Figure 4. Pair distribution functions obtained from the 'mixed' integral equations approach and the Mean Spherical Model for the common parameter  $\sigma=1$  ( $\rho d^3=0.2387$ ) and three values of  $\Gamma$ , as shown.

Contrary to the behaviour of the direct correlation function, the scattering factor  $S(k)=1+\rho\tilde{G}(k)$ , shown in figure 3, displays a shape that roughly interpolates between those of charged points and neutral hard spheres, but is closer to the latter. The relative expansion of  $g(r)$ , compared to  $g(r)$  for uncharged hard spheres, is here reflected in a corresponding compression of  $S(k)$ .

A comparison with the Mean Spherical Model [8] (MSM) is shown in figure 4 for the pair distribution function. In these results the hard-sphere diameter  $\sigma=d/a$  was held fixed at  $\sigma=1.0$ , resulting in a reference hard sphere  $g_0(r)$  which was the same in all three cases and which corresponded to a reduced hard-sphere density  $\rho d^3=0.2387$ . The correction  $\Delta G(r)$  to this  $g_0(r)$  is quite small at  $\Gamma=0.5$ , so that the close agreement shown between the two results in this case masks a larger relative difference in just the correction  $\Delta G(r)$ . Agreement is still relatively good for  $\Gamma=5.0$ , but for the final curve shown at  $\Gamma=50$  the MSM gives qualitatively incorrect results,  $g(r)$  here taking on negative values in the vicinity of the hard core. This breakdown for large  $\Gamma$  is analogous to that of the linearized Debye-Hückel approximation, to which the MSM reduces in the

absence of a hard core. The computed internal energies for the cases shown in figure 4 are  $E/NkT - \frac{3}{2} = -0.341$ ,  $-3.869$ , and  $-47.50$  for the MSM, in order of increasing  $\Gamma$ , and  $-0.341$ ,  $-3.870$ , and  $-42.79$  for the 'mixed' integral equations.

Finally, we hope to have shown that a 'mixed' integral equations approach, wherein the characteristic approximations used in familiar integral equations are applied only with that part of the potential for which each is known to work comparatively well, is a practical one entailing little more complication than a single integral equation.

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