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2002 J. Phys.: Condens. Matter 14 11945

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The application of density functional theory and the generalized mean spherical approximation to double layers containing strongly coupled ions

Dezső Boda¹, Douglas Henderson^{2,5}, Luis Mier y Teran³ and Stefan Sokolowski⁴

¹ Department of Physical Chemistry, University of Veszprém, H-8201 Veszprém, PO Box 158, Hungary

² Department of Chemistry and Biochemistry, Brigham Young University, Provo, UT 84602, USA

³ Departamento de Física, Universidad Autónoma Metropolitana-Iztapalapa, Apartado Postal 55-534, México, DF, CP 09340, Mexico

⁴ Department for the Modeling of Physico-Chemical Properties, MCS University, 20031 Lublin, Poland

E-mail: boda@almos.vein.hu, doug@huey.byu.edu, lmyt@xanum.uam.mx and stefan@paco.umcs.lublin.pl

Received 23 May 2002, in final form 18 July 2002

Published 8 November 2002

Online at stacks.iop.org/JPhysCM/14/11945

Abstract

Density functional theory (DFT) is the most successful simple theory for ions near an electrode (the double layer). However, most previous applications of DFT have been for ions that are relatively weakly coupled. Interesting effects have been found in simulations for ions that are strongly coupled. Specifically, drying of the electrode with a resultant large increase in the magnitude of the adsorption is observed. Further, the capacitance decreases with increasing coupling. The DFT formalism requires the direct correlation function of the bulk electrolyte as input. If the bulk electrolyte is treated by means of the mean spherical approximation (MSA), DFT fails to account for these phenomena. However, if the bulk electrolyte is treated by means of a generalized MSA, partial success results. The electrolyte dries the electrode but the lowering of the capacitance is predicted only weakly. Further refinements are necessary for full success.

1. Introduction

The early density functional theory (DFT) studies of Mier y Teran *et al* [1–3] yielded the first theoretical results, based on a relatively simple theory, that were in good agreement with the Monte Carlo (MC) simulation studies of Torrie and Valleau (TV) [4, 5]. Previously,

⁵ Author to whom any correspondence should be addressed.

to obtain results of this quality it was necessary to employ pair level integral equations for inhomogeneous fluids [6, 7].

Subsequently, Kierlik and Rosinberg (KR) [8] and Rosenfeld (R) [9] have developed equivalent DFT formalisms that are more refined. These too give good agreement with the TV simulations [8–10].

In this paper, we follow TV and the DFT studies and use the restricted primitive model (RPM) where the molecular nature of the solvent is ignored. The electrolytes are assumed to be a fluid of charged hard spheres of equal diameter, d , in a dielectric continuum of dielectric constant ϵ .

It is convenient to define a coupling constant

$$q^* = \sqrt{\frac{\beta z^2 e^2}{\epsilon d}}, \quad (1)$$

where $\beta = 1/kT$ (k is the Boltzmann constant and T is the temperature), e is the magnitude of the electronic charge and z is the magnitude of the valence of the ions. For simplicity, we assume that the charges of the ions are equal (in magnitude). There is no difficulty in applying DFT to ions that are asymmetric in charge. Further, for simplicity we assume a binary electrolyte. The square of the coupling constant is the ratio of the coulombic energy at contact to kT . A large coupling constant can be achieved by a large valence or a small dielectric constant, diameter or temperature, or any combination thereof.

The TV simulations, and most previous applications of DFT, are for small to moderate values of q^* . The MC simulations of Boda *et al* [11, 12] have shown that the properties of the double layer are quite different for large q^* (or small effective temperature, $T^* = 1/q^{*2}$) than for small to moderate q^* . Specifically, the electrode can be dried, the adsorption can be large in magnitude, and the sign of the temperature derivative of the capacitance, C , changes from negative at small q^* (large T^*) to positive at large q^* (small T^*).

The original motivation for the studies of Boda *et al* was to account for the behaviour of molten salt double layers, which have a positive temperature derivative of C that contrasts with the negative temperature derivative for C for electrolytes in solution. A first guess would be that this was a density effect since the density of ions in a molten salt is much higher than for ions in solution. The studies of Boda *et al* showed that the difference in behaviour of C is a ‘temperature’ effect. Both dissolved and molten salt double-layer capacitances have a negative slope at large T^* and a positive slope at small T^* . Small values of T^* occur at room temperatures for molten salts because of their low dielectric constant, $\epsilon \sim 1$. Interestingly, a positive temperature derivative of C is seen experimentally in low concentration electrolytes for so called ‘frozen’ electrolytes [11]. Prior to the work of Boda *et al* [12, 13], the origin of the behaviour of molten salts and frozen electrolytes was not understood.

The well known theory of Gouy and Chapman (GC) is not very accurate but describes qualitatively the behaviour of double layers at small q^* . This is amusing because the GC theory is a theory of point ions, where q^* is infinite. In any case, the GC theory does not exhibit drying or anomalous adsorption under any circumstances and predicts only negative values for dC/dT .

Better theories, such as the mean spherical approximation (MSA), in which the ion diameters are treated in a logically consistent manner, are more accurate than the GC theory for small q^* but are no more successful in predicting the correct behaviour of double layers at large q^* . Even DFT, at least in the early version of DFT used by Mier y Teran *et al* [14], is also unsuccessful.

The origin of the failure of previous studies using DFT lies with their use of the MSA to describe the bulk fluid. If the MSA equation for the density profiles is written in Fourier

transform (FT) language, the FT of the bulk direct correlation function (DCF) appears in the MSA equation for the density profiles. The FT of the DCF for $k = 0$ produces the compressibility of the bulk fluid. It is well known that this MSA compressibility for charged hard spheres is not only unsatisfactory, even for uncharged hard spheres, but fails to include any electrostatic terms. This implies that the electrostatics will be treated unsatisfactorily in the MSA. The effect of using the MSA bulk DCF in DFT is less transparent but it is reasonable to presume that something similar occurs. It will be seen that this is true.

The easiest improvement is to use the generalized mean spherical approximation (GMSA) of Stell and Sun [15] to describe the bulk fluid. This improved treatment of the bulk electrolyte yields a bulk DCF that gives a fairly accurate compressibility. We have already used the MSA with a GMSA treatment of the bulk fluid [16] and obtained improved, but not fully satisfactory, results. The purposes of this paper are to examine DFT with the more modern KR/R formalism and to examine the effect of using the GMSA to describe the bulk fluid together with DFT.

2. Theory

In DFT the grand potential of an inhomogeneous fluid is written using a nonlocal density in the form

$$\Omega = G(\{\rho_i\}) + \frac{1}{2} \sum_i e \int \rho_i(\mathbf{r}) z_i \Phi(\mathbf{r}) \, d\mathbf{r} + \sum_i \int \rho_i [v_i(\mathbf{r}) - \mu_i] \, d\mathbf{r}, \quad (2)$$

where $\rho_i(\mathbf{r})$ are the ionic densities and μ_i are the chemical potentials, $v_i(\mathbf{r})$ is the nonelectrostatic part of the external potential that defines the electrode, $G(\{\rho_i\})$ is a free energy density functional and $\Phi(\mathbf{r})$ is the mean electrostatic potential that is determined from Poisson's equation,

$$\nabla^2 \Phi(\mathbf{r}) = -\frac{4\pi e}{\epsilon} \sum_i z_i \rho_i(\mathbf{r}) \quad (3)$$

where $\rho_i(\mathbf{r}) = \rho_i g_i(\mathbf{r})$.

The functional $G(\{\rho_i\})$ is expanded in a functional Taylor series in powers of $\Delta\rho_i(\mathbf{r}) = \rho_i(\mathbf{r}) - \rho_i$, where ρ_i is the ionic density of the homogeneous electrolyte. Thus,

$$\begin{aligned} G[\{\rho_i\}] = & F_{id}[\{\rho_i\}] + \int g^{ex}(\{\rho_i\}) \, d\mathbf{r} + \sum_i (\mu_i^{ex} - z_i e \Phi_{bulk}) \int \Delta\rho_i(\mathbf{r}) \, d\mathbf{r} \\ & - \frac{kT}{2} \sum_{i,j} \int c_{ij}^{sr}(|\mathbf{r} - \mathbf{r}'|) \Delta\rho_i(\mathbf{r}) \Delta\rho_j(\mathbf{r}') \, d\mathbf{r} \, d\mathbf{r}' + \dots, \end{aligned} \quad (4)$$

where $c_{i,j}^{sr}$ is the the short range part of the DCF,

$$c_{ij}^{sr}(r) = c_{ij}(r) + \frac{\beta z_i z_j e^2}{\epsilon r}, \quad (5)$$

$F_{id}(\{\rho_i\})$ is the ideal part of the free energy of the bulk solution and μ_i^{ex} and $g^{ex}(\{\rho_i\})$ are the excess chemical potential and excess Helmholtz energy density of the homogeneous solution less the electrostatic energy.

Summing the hard sphere contributions to all orders, we obtain

$$\begin{aligned} G(\{\rho_i\}) = & F_{HS}(\{\rho_i\}) + \int [g^{ex}(\{\rho_i\}) - f_{HS}^{ex}(\{\rho_i\})] \, d\mathbf{r} \\ & + \sum_i (\mu_i^{ex} - \mu_{i,HS} - z_i e \Phi_{bulk}) \int \Delta\rho_i(\mathbf{r}) \, d\mathbf{r} \\ & + \frac{kT}{2} \sum_{i,j} \int \Delta c_{ij}(|\mathbf{r} - \mathbf{r}'|) \Delta\rho_i(\mathbf{r}) \Delta\rho_j(\mathbf{r}') \, d\mathbf{r} \, d\mathbf{r}', \end{aligned} \quad (6)$$

where $\mu_{i,HS}$ and f_{HS}^{ex} are the chemical potential and excess Helmholtz energy densities of the homogeneous hard sphere fluid.

Requiring that the grand potential be minimized, $\delta\Omega/\delta\rho_i(r) = 0$, gives the equation

$$\frac{\delta G}{\delta\rho_i(\mathbf{r})} + z_i e\Phi(\mathbf{r}) + v_i(\mathbf{r}) = \mu_i \quad (7)$$

and leads to an integral equation involving the bulk DCF,

$$\begin{aligned} -kT \ln[\rho_i(\mathbf{r})/\rho_i] = & v_i(\mathbf{r}) + \left[\frac{\delta F_{HS}^{ex}}{\delta\rho_i(\mathbf{r})} - \mu_{i,HS}^{ex} \right] + z_i e[\Phi(\mathbf{r}) - \Phi_{bulk}] \\ & - kT \sum_j \int \Delta c_{ij}(|\mathbf{r} - \mathbf{r}'|) \Delta\rho_j(\mathbf{r}') d\mathbf{r}', \end{aligned} \quad (8)$$

for the density profile. As a result, the inhomogeneous fluid is constrained to be in equilibrium with the bulk fluid that is specified by the DCF. Although it is not necessary that the bulk fluid be described analytically, it is certainly convenient if this is the case.

The MSA is a convenient analytic theory for charged hard spheres (the model of the electrolyte used here). The MSA DCF for a homogeneous mixture of charged hard spheres, all of the same diameter, is [17, 18]

$$c_{ij}(R) = \begin{cases} -a - br - \frac{\eta}{2} ar^3 - \frac{\beta z_i z_j e^2}{\epsilon d} [2B - B^2 r], & R < d \\ -\frac{\beta z_i z_j}{\epsilon r}, & R > d, \end{cases} \quad (9)$$

where $r = R/d$, $B = \Gamma d/(1 + \Gamma d)$ and Γ is related to the Debye inverse length

$$\kappa^2 = \frac{4\pi\beta z^2 e^2 \rho}{\epsilon}, \quad (10)$$

by

$$\kappa = 2\Gamma(1 + \Gamma d), \quad (11)$$

where ρ is the number density of *all* the charged spheres. The parameters a and b are

$$a = \frac{(1 + 2\eta)^2}{(1 - \eta)^4}, \quad (12)$$

and

$$b = -6\eta \frac{(1 + \eta/2)^2}{(1 - \eta)^4}, \quad (13)$$

where $\eta = \pi\rho d^3/6$. If equation (9) is used as input into equation (8), the resulting theory may be called the DFT/MSA theory. This is the version of DFT that has been used previously. As we will now point out, the use of the MSA can lead to problems.

If the thermodynamic properties of the electrolyte are obtained from the MSA, the best result comes from the energy equation. This result is

$$\frac{pV}{NkT} = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3} - \frac{(\Gamma d)^3}{3\pi\rho d^3}. \quad (14)$$

As is common, the MSA is not self-consistent. Different expressions for the pressure are obtained from different routes. Even worse, the compressibility equation, which results from an integration of the MSA DCF, yields

$$\beta \frac{\partial p}{\partial \rho} = \frac{(1 + 2\eta)^2}{(1 - \eta)^4}, \quad (15)$$

which does not even include any electrostatic terms and, thus, is independent of q^* or T^* . We believe that this is the source of at least some of the problems with the previous applications (by ourselves and others) of the DFT/MSA for inhomogeneous charged hard spheres.

A relatively easy improvement is obtained by using the GMSA of Stell and Sun [15] for the bulk DCF of the charged hard spheres. In the GMSA, a Yukawa function is added to the DCF of the bulk system of charged hard spheres outside the core. This forces a modification of the DCF inside the core. The resulting expression for the DCF is

$$c_{ij}(R) = \begin{cases} -a - br - \frac{\eta}{2}ar^3 - v\frac{1 - e^{-zr}}{zr} - v^2\frac{\cosh zr - 1}{2\kappa z^2 e^2 r} \\ \quad - \frac{\beta z_i z_j e^2}{\epsilon d} [2B - B^2 r], & R < d \\ -\frac{\beta z_i z_j}{\epsilon r} + \frac{K e^{-z(r-1)}}{r}, & R > d. \end{cases} \quad (16)$$

The parameter B is given by $B = \Gamma d / (1 + \Gamma d)$, as before; however, because of the Yukawa function, a and b differ from equations (12) and (13). The parameters a , b and v are complex functions of K , z and η that are given in a paper of Waisman [19] (that contains a misprint) and in subsequent papers by Henderson *et al* [20] and Høye and Stell [21]. In the GMSA, K and z are chosen so that the compressibility, pressure and energy routes all yield equation (14).

This improvement yields not just better thermodynamic functions but also improved correlation functions, as can be seen from the figures of Stell and Sun [15]. However, it is to be expected that the GMSA will be only a partial success in application to the double layer because the correlation functions of all pairs are treated in exactly the same way. Since the capacitance is the result of the differences in the manner in which the different species of ions respond to the electrode charge, we expect that the use of the GMSA DCFs will result in small or no changes in the capacitance. This has already been seen in our previous MSA/GMSA study where the GMSA is used to describe the bulk electrolyte and the MSA is used to describe the inhomogeneous fluid. Even so the use of the GMSA leads to partial success. For example, drying is described.

Here the GMSA is used as input into DFT, yielding a DFT/GMSA theory. In this paper, both the DFT/MSA and DFT/GMSA theories are studied using KR/R formalism.

3. Results

The density profiles, resulting from DFT/MSA and DFT/GMSA, are shown at relatively small T^* for a low density ($\rho^* = 0.04$) in figure 1 and for a high density ($\rho^* = 0.65$) in figure 2. The density used in figure 1 is typical of an electrolyte solution whereas the density used in figure 2 is typical of a molten salt. Firstly, drying is expected only for densities that are close to the critical point of the electrolyte. This can be seen from the exact contact value condition (CVC) [22]

$$kT \sum_i \rho_i(d/2) = p + \frac{2\pi\sigma^2}{\epsilon}, \quad (17)$$

where p is the pressure of the bulk fluid and σ is the charge of the electrode. Drying will occur when the charge of the electrode is not too great and at low densities and small T^* , where p is small.

From figure 1 it is seen that the DFT/MSA does not exhibit drying. This was seen earlier in our earlier study based on an earlier DFT formalism and confirms our claim that the use of the earlier DFT formalism did not affect our conclusions. In contrast, the DFT/GMSA is

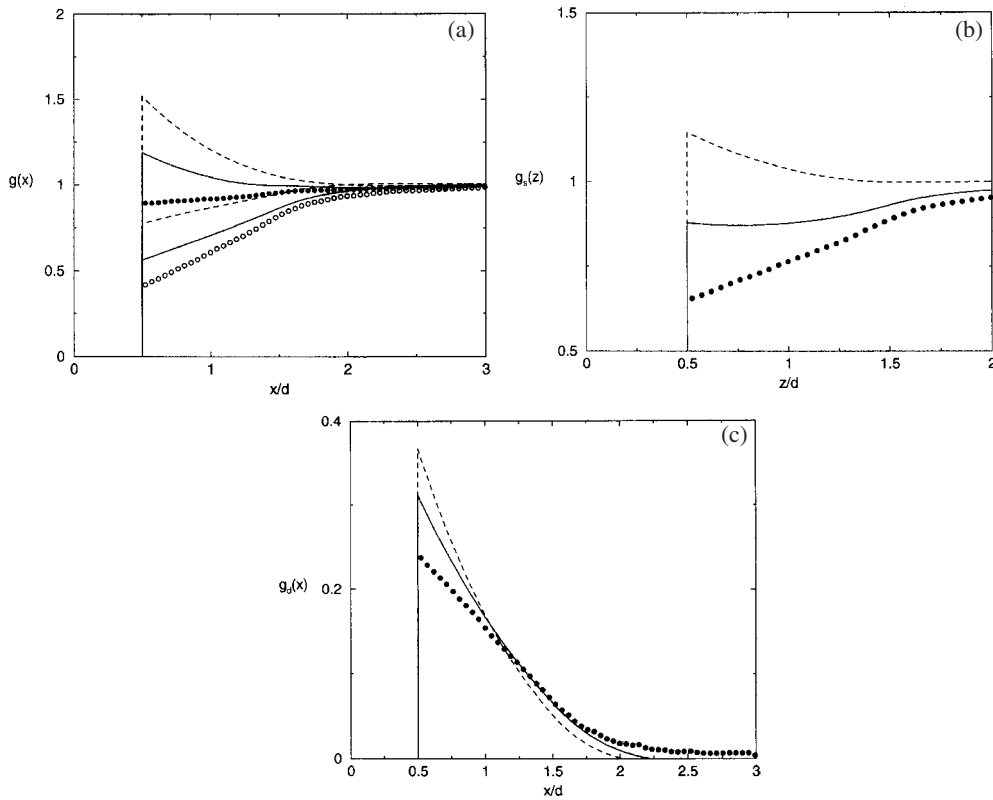


Figure 1. Density profiles for charged hard spheres ($\rho d^3 = 0.04$) near a charged hard surface ($\sigma d^2/e = 0.00765$) for $T^* = 0.15$. The profiles are plotted in part (a) and $g_s(x)$ and $g_d(x)$ are plotted in parts (b) and (c). The MC values are given by the circles (solid for counterions and open for coions in part (a)). The solid and dashed curves give the DFT/GMSA and DFT/MSA results.

somewhat more successful. Drying is observed but not as much as in the simulations. This is a step forward from the MSA/MSA (i.e., MSA is used for both the bulk and the interface) where

$$kT \sum_i \rho_i(d/2) = \sqrt{\beta \frac{\partial p}{\partial \rho}}, \quad (18)$$

with $\beta \partial p / \partial \rho$ being given by equation (15). Note that the MSA/MSA result is independent of q^* and the electrode charge and there is no drying. The DFT seems to satisfy the CVC theorem but with something related to p substituted for the first term on the RHS in equation (17). Thus, as can be seen from figure 1(b), where $g_s(x) = \sum g_i(x)$ is plotted, the simulation values for $g_s(x)$ are significantly smaller than the the DFT values. The DFT/GMSA results are better than the DFT/MSA results but are only partially successful.

The difference of the profiles $g_d(x)$ is plotted in figure 1(c). Again the DFT/GMSA are intermediate between the DFT/MSA and MC results. The drying, already seen in figures 1(a) and (b), depends on the species. As a result, the DFT/GMSA $g_d(x)$ has a longer range than does the DFT/MSA $g_d(x)$. The MC values have an even longer range. As we shall see shortly, this causes the MC capacitance to be smaller than the DFT/GMSA result, which is smaller than the DFT/MSA result.

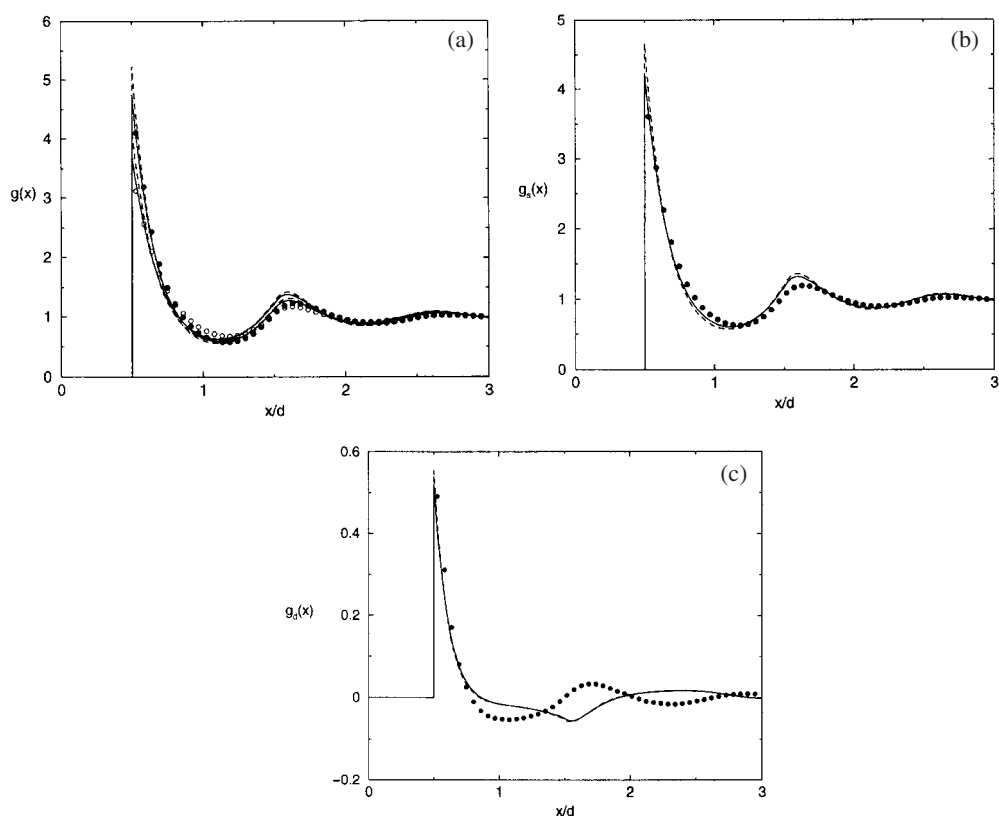


Figure 2. Density profiles for charged hard spheres ($\rho d^3 = 0.64$) near a charged hard surface ($\sigma d^2/e = 0.0234$) for $T^*0.211$. Parts (a)–(c) and the points and curves have the same meaning as in figure 1.

Both the DFT/MSA and DFT/GMSA profiles that are plotted in figure 2 for the molten salt case are improvements over the earlier DFT/MSA results. The oscillations of both sets of DFT curves are closer to being in phase with those of the simulation curves than are the earlier DFT results. For molten salts, the function $g_s(x)$ does not exhibit drying because $p > \rho kT$. However, as is seen in figure 2(b), $g_s(x)$ is given fairly accurately by both DFT/MSA and DFT/GMSA. The DFT/GMSA values near contact are slightly more accurate than the DFT/MSA values. In contrast, in the earlier version of DFT/MSA, the profiles were markedly out of phase with the MC results.

On the other hand, there is almost no difference in $g_d(x)$ between the two versions of DFT. In both versions of DFT, there are too many counterions near the electrode. Even though there is no drying seen in $g_s(x)$, the values of $g_d(x)$ exhibit differential drying, as compared with simpler theories such as the GC theory and MSA.

Further insight is gained from the contact values at zero electrode charge that are plotted in figures 3 and 4 for $\rho d^3 = 0.04$ and $\rho d^3 = 0.64$. Note that the DFT/MSA contact values are independent of q^* and T^* , reflecting the fact that the MSA compressibility equation of state, equation (15), is independent of q^* and T^* . As a result, the CVC agrees qualitatively with equation (18). The DFT/GMSA contact values in figure 3 are intermediate between the GMSA pressure, obtained from equation (1), and the simulation values. It would be a mistake to make

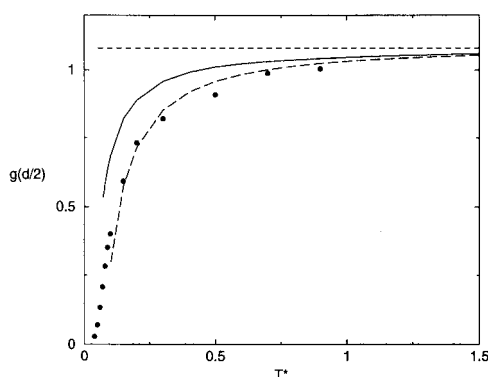


Figure 3. Contact values of the density profile, $g(d/2)$ for $\rho d^3 = 0.04$ for an uncharged hard surface. The circles give the MC values. The solid curve gives pV/NkT . The long and short dashed curves give the DFT/GMSA and DFT/MSA results.

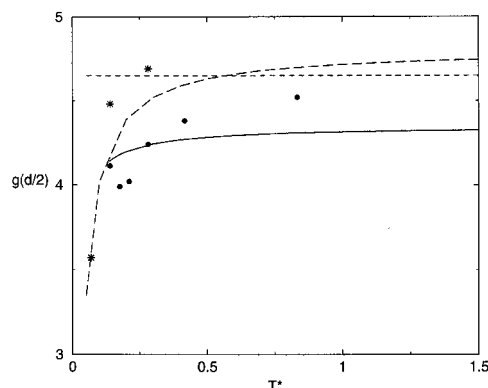


Figure 4. Contact values of the density profile, $g(d/2)$ for $\rho d^3 = 0.64$ for an uncharged hard surface. The points given by asterisks are the simulation values of Larsen and Rodege [23] for pV/NkT . The other points and curves have the same meaning as in figure 3.

too much of this. If the DFT/GMSA were fully self-consistent, the DFT/GMSA contact values would agree with the GMSA values of p . The fact that the DFT contact values in figure 3 are intermediate between equation (14) and the MC values is probably only a coincidence, as seen in figure 4. For comparison, some simulation values, due to Larsen and Rodege [23], of βp for molten salts are given in figure 4.

The established folklore is that DFT satisfies the CVC exactly. However, the evidence is anecdotal at best. It is our belief that DFT does give the factor $2\pi\sigma^2/\epsilon$ in CVC, exactly, as do some other theories. This is important because it does mean that the electrostatics of the electrode has been treated correctly. However, our belief is that if the DFT/MSA is used, some function of the hard sphere MSA compressibility, given by equation (14), appears in the CVC instead of p and, if the DFT/GMSA is used, some function of the GMSA pressure, given by equation (15), but not the pressure itself, appears in the CVC. We have been unable to establish on the basis of our numerical results what are these functional relationships. It would be useful if some definitive answer to this question were available.

Finally, in figures 5 and 6, the capacitance is plotted for $\rho d^3 = 0.04$ and 0.64 , respectively. The DFT/MSA values are similar to our previous DFT results, validating our claim that the use of the earlier DFT gave qualitatively correct results for the DFT/MSA approach. The DFT/MSA and DFT/GMSA capacitances are virtually identical at $\rho d^3 = 0.64$. However, for $\rho d^3 = 0.04$, the DFT/GMSA capacitance exhibits very slightly more correct behaviour. The DFT/GMSA capacitance does level off and the temperature derivative seems to reverse sign. This was beyond our expectations. Evidently, even though the GMSA DCF of all species pairs are treated equally, the DFT/GMSA profiles of different species can be affected slightly differently. Possibly this is due to slight nonlinear effects, even though the electrode charge is small.

For the molten salt density, the DFT values of C are greater than the earlier DFT/MSA values, even at small q^* . Evidently, the improved profiles of this work, seen in figure 2, over those of our earlier work, seen in figure 4 of [13], have come at a cost.

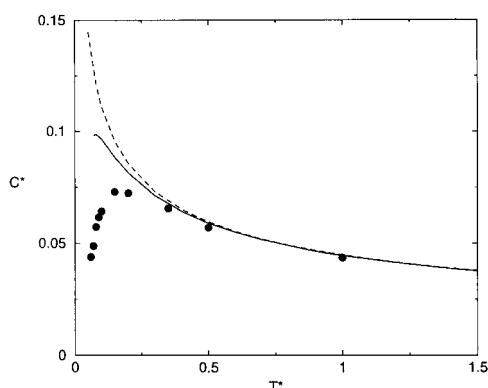


Figure 5. Integral capacitance, $C^* = \sigma^*/\psi^*$, where $\psi^* = \beta e\psi$ and ψ is the electrode voltage, for charged hard spheres ($\rho d^3 = 0.04$) near a hard surface with a small charge. The circles and curves have the same meaning as in figure 3.

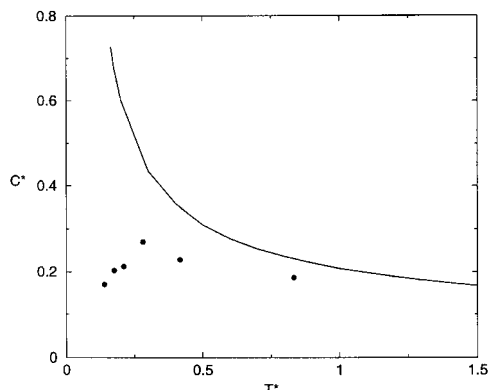


Figure 6. Integral capacitance, C^* , as defined in the caption of figure 5, for charged hard spheres ($\rho d^3 = 0.64$) near a hard surface with a small charge. The circles and curves have the same meaning as in figure 3.

4. Conclusions

The DFT/MSA approach is similar to the MSA/MSA approach. The use of the bulk MSA as input does not lead to any of the interesting behaviour of the double layer at small T^* (or large q^*). This we believe is due to the fact that the MSA compressibility, which is closely related to the DCF, is both different from the pressure and independent of T^* .

In contrast, the DFT/GMSA, and the MSA/GMSA, correctly place the pressure, or a related quantity, in the CVC and so can account for drying when p is small. For reasons that are unclear, MSA/GMSA places the MSA pressure in the CVC whereas DFT/GMSA seems to place only a related quantity in the CVC. As a result, the MSA/GMSA and DFT/GMSA can account for the drying seen at small T^* . Both will predict the large negative adsorption near the critical point that is associated with drying. We did not study this latter phenomenon here because it will be less dramatic than is the actual case, because, as seen in figure 3, the drying in the present version of DFT/GMSA is rather less than should be the case.

The MSA/GMSA and DFT/GMSA fail to account for the small values of C seen at small T^* . This is because the GMSA of Stell and Sun, that we use, treats all the DCFs of the bulk electrolyte in the same way. To obtain better results for the capacitance a different Yukawa function should be added to the DCFs for like and unlike pairs. The formalism is straightforward but as yet no recipe for the resultant A_{ij} and z_{ij} is available. We intend to pursue this question.

In a recent paper with Holovko [24], we examined the effect of ion pairing in the electrolyte upon the capacitance. We found that the ion pairing causes the capacitance to decrease at low T^* . This is, of course, hardly surprising since ion pairing will cause drying. Drying and ion pairing are aspects of the same phenomenon. In principle, an ion pairing version of DFT (IPDFT) could be formulated. However, even when formulated, IPDFT would be difficult to implement since the solution of the bulk MSA for ion pairing (IPMSA) is incomplete. The IPMSA correlation functions are not yet available and no results for molten salts have been obtained from the IPMSA. In any case, the DFT/GMSA and IPDFT/IPMSA should converge on the same results. Any theory giving correct thermodynamics should reflect ion pairing, explicitly or implicitly.

Finally, we comment that although our main interest has been for small values of T^* , the large deviations seen by TV [5], and ourselves [24], for double layers containing divalent salts is but the onset of the phenomena seen here. The development of improved theories for small T^* will lead also to improved predictions for aqueous systems at larger T^* and to improved predictions for frozen electrolytes and molten salts.

Acknowledgments

This work was supported in part by the National Science Foundation (grant No CHE98-13729), NATO (grant No HTECH CRG972915) and the Hungarian National Research Fund (OTKA-F035222).

References

- [1] Mier y Teran L, Suh S H, White H S and Davis H T 1990 *J. Chem. Phys.* **92** 5087
- [2] Tang Z, Mier y Teran L, Davis H T, Scriven L E and White H S 1990 *Mol. Phys.* **71** 369
- [3] Mier y Teran L, Tang Z, Davis H T, Scriven L E and White H S 1991 *Mol. Phys.* **72** 817
- [4] Torrie G M and Valleau J P 1980 *J. Chem. Phys.* **73** 5807
- [5] Torrie G M and Valleau J P 1982 *J. Phys. Chem.* **86** 3251
- [6] Plischke M and Henderson D 1988 *J. Chem. Phys.* **88** 2712
- [7] Plischke M and Henderson D 1989 *J. Chem. Phys.* **90** 5738
- [8] Kierlik E and Rosinberg M L 1991 *Phys. Rev. A* **44** 5025
- [9] Rosenfeld Y 1993 *J. Chem. Phys.* **98** 8126
- [10] Patra C N and Ghosh S K 1993 *Phys. Rev. E* **47** 4088
- [11] Hamelin A, Rottgermann S and Schmickler W 1987 *J. Electroanal. Chem.* **230** 281
- [12] Boda D, Henderson D and Chan K-Y 1999 *J. Chem. Phys.* **110** 5346
- [13] Boda D, Henderson D, Chan K-Y and Wasan D T 1999 *Chem. Phys. Lett.* **308** 473
- [14] Mier y Teran L, Boda D, Henderson D and Quinones-Cisneros S 2001 *Mol. Phys.* **99** 1323
- [15] Stell G and Sun S F 1975 *J. Chem. Phys.* **63** 5333
- [16] Henderson D, Boda D and Wasan D T 2000 *Chem. Phys. Lett.* **325** 655
- [17] Waisman E and Lebowitz J L 1970 *J. Chem. Phys.* **52** 4307
- [18] Waisman E and Lebowitz J L 1972 *J. Chem. Phys.* **56** 3093
- [19] Waisman E 1973 *Mol. Phys.* **25** 45
- [20] Henderson D, Stell G and Waisman E 1975 *J. Chem. Phys.* **62** 4247
- [21] Høye J S and Stell G 1977 *J. Chem. Phys.* **67** 524
- [22] Henderson D, Blum L and Lebowitz J L 1979 *J. Electroanal. Chem.* **102** 315
- [23] Larsen B and Rodge S A 1978 *J. Chem. Phys.* **68** 1309
- [24] Holovko M, Kapko V, Henderson D and Boda D 2001 *Chem. Phys. Lett.* **341** 363
- [25] Boda D, Fawcett W R, Henderson D and Sokolowski S 2002 *J. Chem. Phys.* **116** 7170