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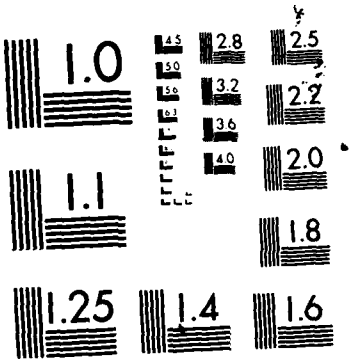

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Abstract (Cont.)

derivative of the free energy with respect to the density

$$F = \rho^2/2 \; \partial^2 f(\rho,T)/\partial\rho^2|_T$$

The function η (F) as obtained from MHNC calculations for bulk simple fluids is found to be remarkably independent of the pair potential. As an example for the accuracy fo the resulting method, the one component plasma near a hard wall is discussed.

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FLUIDS IN CONTACT WITH A HARD SURFACE: UNIVERSALITY OF THE BRIDGE FUNCTIONS FOR THE DENSITY PROFILE

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FLUIDS IN CONTACT WITH A HARD SURFACE:UNIVERSALITY OF THE BRIDGE FUNCTIONS FOR THE DENSITY PROFILE

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ABSTRACT

The modified hypernetted chain theory (MHNC) for density profiles of fluids in contact with a hard, smooth surface is found to posess a remarkably simple and interesting property: The accuracy of the MHNC and the universality of the bridge functions for the density profiles can be tested without resort to any detailed solution of the integral equations. It is given by the degree of universality of the bulk bridge parameter (e.g. η for the Percus-Yevick hard-sphere bridge function) when expressed in terms of the second partial derivative of the free energy with respect to the density

$$F = -\rho^2/2 \quad \partial^2 f(\rho,T)/\partial\rho \,|_T$$

The function η (F) as obtained from MHNC calculations for bulk simple fluids is found to be remarkably independent of the pair potential. As an example for the accuracy of the resulting method, the one component plasma near a hard wall is discussed.

I-INTRODUCTION

The pair correlation functions and the equation of state of bulk are given with a high degree of accuracy by the MHNC,which is based on the universality of the short ranged part of the bridge functions [1]. However, a similarly accurate theory for the inhmogeneous fluid is not yet available.In particular this is the case of the interface of a ionic solution near a charged,smooth hard wall [2].This is a simple,highly idealized model of the interface of a ionic fluid and a charged solid but it has been extensively used in electrochemistry [3].Recently,as part of an extensive study of the one component plasma (OCP) [4],the interfacial properties of the OCP and hard surfaces [5-8] were studied.

The comparison between the accuracy of the same approximation in the bulk or at the interface shows that in general,a good approximation for the bulk phase is not as succesful for the interface.For example, the HNC is an excellent theory for the bulk electrolytes and OCP [1,4] However it is a much poorer theory for the charged interface.The reason is that it underestimates the density oscillations caused by the excluded volume effects.The error produced by this underestimation is much more serious for the flat interface case.The inclusion of bridge diagrams corrects in part this defficiency, and should yield a much more accurate theory for the interface.

As a first step in the systematic improvement of the flat wall HNC similar to what has been done in the bulk case [1], the present paper provides a proof of the universality of the short ranged part of the bridge functions for the density profiles near a flat, smooth interface.The analysis of the MHNC scheme,and the availability of MHNC results for the bulk OCP enables us to establish this result without having to particularize to any specific density profile in

detail. For the restricted (dielectric continuum) primitive model of ionic solutions a similar analysis is also possible.

A fluid in contact with an impenetrable wall can be considered [9] as a limiting case of a mixture in which one of the components (which we label w) grows in size but dwindles in concentration, so that the properties of the bulk phase of the fluid remain unchanged. Let R_w be the hard core radius of the w particle (the "wall"), with density ρ_w. Then the limit is [9,10]

$$\rho_w \to 0 \quad ; \; R_w \to \infty \quad \text{and} \quad \rho_w R_w^3 \to 0.$$

We use the Ornstein Zernike (OZ) equation as our starting point. We show that in the planar limit the bridge functions of the MHNC approximation can be determined from a universal function. The criterion to determine the parameters of this function are given in section II. The remarkable (but perhaps not unexpected) fact is that nearly all the bridge function parameters are already determined by the solution of the bulk MHNC equations. The only free parameter turns out to be a shift parameter, λ, which determines the position of the wall in the reference system relative to that of the system under consideration. This special property of the bridge functions, when analyzed in the context of the sum rules for the density profiles (discussed in section III), leads to a remarkably simple and interesting result : The accuracy of the MHNC theory and the universality of the bridge functions for the density profiles, can be tested without having to solve the equations. It is given by the degree of universality (i.e. the independence of the pair potential) of the bulk bridge parameters (for example, η of the Percus-Yevick hard sphere functions), when expressed in terms of the second partial derivative of the excess free energy with respect to η.

This test is performed in section IV,where the universality is shown to be very accurate.(see figure 1).As an example of the resulting method and its accuracy we consider in section V the density profile of the OCP near a flat wall.The Percus Yevick hard sphere bridge functions for the density profiles are briefly discussed in section VI while some implications of the present work are mentioned in the concluding section VII.

II-Ornstein-Zernike Equation and MHNC Closures in the Planar Limit

Consider a mixture of particles labelled 1,2,..m,w ,with total density

$$\rho=\sum_{i=1}^{m+1} N_i/V=N/V,$$

temperature $\beta=(k_B T)^{-1}$,and mole fractions $x_i=N_i/N$,$x_w=N_w/N$.In the limit $x_w\to 0$ the OZ equation decouples into two parts [9]:the bulk part

$$h_{ij}(\underset{\sim}{r})=c_{ij}(\underset{\sim}{r}) +\rho\sum_{\ell=1}^{m} x_\ell\int d\underset{\sim}{r}'h_{i\ell}(|\underset{\sim}{r}-\underset{\sim}{r}'|)c_{\ell j}(\underset{\sim}{r}') \qquad (2.1)$$

and the wall part

$$h_{wi}(\underset{\sim}{r})=c_{wi}(\underset{\sim}{r}) +\rho\sum_{\ell=1}^{m} x_\ell\int d\underset{\sim}{r}'h_{w\ell}(|\underset{\sim}{r}-\underset{\sim}{r}'|)c_{\ell i}(\underset{\sim}{r}') \qquad (2.2)$$

where $h_{ij}(\underset{\sim}{r})$ is the total correlation function, and $c_{ij}(\underset{\sim}{r})$ is the direct correlation function for the bulk fluid. $h_{wi}(\underset{\sim}{r})$ and $c_{wi}(\underset{\sim}{r})$ are the correlations involving the w particle.Consider now the planar limit: let $r=R_w+x$ (eventually $R_w\to\infty$) and denote

$$h_{wi}(r) \to h_i(r)$$

$$c_{wi}(r) \to c_i(r)$$

Then [9]

$$h_i(x)=c_i(x) +\rho\sum_{\ell=1}^{m} x_\ell 2\pi\int_{-\infty}^{\infty}dt\, h_\ell(t)\int_{|x-t|}^{\infty}ds\quad s c_{\ell i}(s) \qquad (2.2')$$

where we are implicitly using hard core exclusion conditions for the wall

$$g_i(x)=h_i(x) +1=0, \qquad x<R_i \qquad (2.3)$$

where R_i is the radius of the hard core of i.

The fluid now occupies the right half space, x>0, and $\rho x_i g_i(x)$ gives the probability of finding the center of particle i at a distance x from the surface of the wall. The function $g_i(x)$ represents, therefore, the density profile. When the wall is charged and the system has ions, then (2.2') has to be modified to avoid divergencies produced by the Coulomb potential [11]

$$\int_{|x-t|}^{\infty} ds \quad sc_{\ell i}(s) \rightarrow \int_{|x-t|}^{\infty} ds \quad sc_{\ell i}^{SR}(s) + \beta Q_i Q_\ell (|x-t|+x+t) \qquad (2.2'')$$

where

$$sc_{\ell i}^{SR}(s) = sc_{\ell i}(s) + \beta Q_i Q_\ell / s \qquad (2.4\ )$$

The charged system must satisfy the bulk electroneutrality condition

$$\sum_{i=1}^{m} x_i Q_i = 0 \qquad (2.5)$$

and the wall electroneutrality condition

$$\rho \sum_{i=1}^{m} x_i Q_i \int dx \; g_i(x) = -E_o/4\pi \qquad (2.6)$$

where E_o is the electric field at the surface of the wall.

The exact diagrammatic expansion of the fluid pair correlation functions supplements the OZ equation with the closures [1,4]

$$\log(1+h_{ij}(r)) = -[\beta\phi_{ij}(r) + B_{ij}(r)] + [h_{ij}(r) - c_{ij}(r)]$$
$$i,j = 1 \ldots m, w \qquad (2.7)$$

where $\phi_{ij}(r)$ are the pair interaction potentials, and the bridge functions $B_{ij}(r)$ are given in terms of diagrams containig $h_{ij}(r)$ bonds.

The hypernetted chain approximation HNC is obtained by setting $B_{ij}(r)=0$. Note also that (2.7) is an HNC for the effective potential $\phi_{ij}(r)+B_{ij}(r)/\beta$. Presently, the MHNC is the most accurate theory available for the pair correlation functions of the fluid[1,12-16]. The MHNC scheme is based on the short range universality of the bridge functions: In practice, one considers a reference system (superscript 'o') of hard spheres of radii R°_i, R°_w, with the same relative concentrations $x_i x_w$, temperature β and density ρ as the original system. The basic MHNC approximation is

$$B^{MHNC}_{ij}(r) = B_{ij}(r, R^\circ, \ldots, R^\circ_m, R^\circ_w) \qquad (2.8)$$

where the reference hard core radii R°_i, R°_w are adjustable parameters to be determined by imposing consistency criteria. In particular, the following MHNC 'virial-energy' consistency requirement can be imposed locally [13-16] (without having to consider different temperatures or densities) as a set of m+1 equations for the m+1 unknown radii $R^\circ(\beta,o)$:

$$\sum_{i,j=1,\cdots m,w} x_i x_j \int d\underset{\sim}{r}\, [\, g_{ij}(\underset{\sim}{r}) - g^\circ_{ij}(\underset{\sim}{r})]\, \partial B_{ij}(r)/\partial R^\circ_k = 0 \qquad k=1,..m,w \qquad (2.9)$$

The HNC, with $B_{ij}=0$, is the member of the lowest order of this class of approximations satisfying 'virial-energy' consistency [13,14,17].

Detailed results [1,12-16,18-21] show that the MHNC reproduces the computer simulation results for a large variety of fluids within the statistical error of the simulations. The results for multicomponent classical plasmas are nearly as accurate [12], while somewhat less accurate results are obtained for electroytes and molten salts [20]. In any event, the MHNC results in a significant improvement of the HNC theory. The accuracy of the local MHNC theory based on the universality

of the bridge functions (2.8,2.9), and its relation to the variational perturbation theory for the equation of state, were recently studied in detail [13-14].

The interesting feature of the planar limit is that the closures (2.7) decouple from the bulk part in the same way as the OZ equation:

$$\log(1+h_{ij}(r)) = -[\beta\phi_{ij}(r)+B_{ij}(r)]+[h_{ij}(r)-c_{ij}(r)] \qquad i,j=1\ldots m \tag{2.10}$$

and for the wall part

$$\log(1+h_i(x)) = -[\beta\phi_i(x)+B_i(x)]+[h_i(x)-c_i(x)] \qquad i=1\ldots m \tag{2.11}$$

where $\phi_{wi}(r) \rightarrow \phi_i(x)$, $B_{wi}(r) \rightarrow B_i(x)$.

When employing the MHNC scheme for the bulk part, eqs. (2.8,9) remain unchanged, except that the w component is not taken into account. In other words, we get the usual MHNC bridge functions for the bulk phase with the m bridge parameters $R_i^\circ(\beta,\rho)$. Taking the planar limit in the reference system (using now $r=R_w^\circ+z=R_w+\lambda+x$), we obtain the reference bridge functions

$$g_{wi}^\circ(r) \rightarrow g_i^\circ(z) = g_i^\circ(x+\lambda, R_1^\circ(\beta,\rho), \ldots R_m^\circ(\beta,\rho))$$

$$B_{wi}^\circ(r) \rightarrow B_i^\circ(z) = B_i^\circ(x+\lambda, R_1^\circ(\beta,\rho), \ldots R_m^\circ(\beta,\rho)) \tag{2.12}$$

so that the (m+1)th equation in (2.9) becomes

$$\sum_{i=1}^{m} x_i \int dx\, [\, g_i(x) - g_i^\circ(x+\lambda)]\, \partial B_i^\circ(x+\lambda)/\partial\lambda = 0 \qquad i=1,\ldots m \tag{2.13}$$

from which we find the remaining bridge parameter (the shift parameter)

$$\lambda = \lim_{R_w, R^\circ_w \to \infty} (R^\circ_w - R^\circ_w) \tag{2.14}$$

In other words, the bulk part of the MHNC scheme determines all the radii $R^\circ_i(\beta, \rho)$ and the planar reference functions $g^\circ_i(z)$ and $B^\circ_i(z)$. The only remaining free parameter of the MHNC is the shift λ, which should be the same for all components of the mixture. This special feature has significant consequences to be discussed below.

Finally, it should be noted that although it is presently impossible to calculate, the non-additive diameter case gives more flexibility to the scheme. In that case, instead of (2.13), we get the system of equations for the m shift parameters λ_i:

$$\int dx \, [\, g_i(x) - g^\circ_i(x+\lambda_i)] \, \partial B^\circ_i(x+\lambda_i)/\partial\lambda_i = 0 \qquad i=1,..m \tag{2.15}$$

III-MHNC Equations for the Density Profiles and Bridge Functions: Sum Rules

Combining (2.2") and (2.11) we arrive at the following equations for the density profiles:

$$\log[1+h_i(x)] = \rho\sum_{\ell=1}^{m} x_\ell 2\pi \int_{-\infty}^{\infty} dt\, h_\ell(t) \int_{|x-t|}^{\infty} ds\, s c_{\ell i}^{sR}(s) - \beta Q \Psi_i(x) - \beta \phi_i^{s\ell}(x) - b_i(x), \quad x \geq R_i \tag{3.1}$$

$$[1+h_i(x)] = 0, \quad x < R_i$$

where $\Psi(x)$ is the electrostatic potential in the half space $x \geq 0$

$$\Psi(x) = 4\pi\rho \int_x^{\infty} dt\, (x-t) \sum_\ell x_\ell Q_\ell h_\ell(t) \tag{3.2}$$

which satisfies the boundary conditions

$$\partial\Psi/\partial x \Big|_{x=0} = -E_0 \qquad ; \Psi(x \to \infty) = 0 \tag{3.3}$$

$\phi_i^{s\ell}(x)$ is the non-electrostatic ,non-hard core part of the interaction between particle i and the wall.Eqs (3.1-3) also apply to the situation when the system is immersed in a uniform neutralizing background of charge density ρ_b : It this case, however, (2.5) and (2.6) have to be modified

$$\rho \sum_{i=1}^{m} x\, Q = -\rho_b \tag{3.4}$$

$$\rho \sum_{i=1}^{m} x_i Q_i \int dx\, h_i(x) = -E_0/4\pi \tag{3.5}$$

When the bridge functions of a reference system are employed, then using the property

$$\partial B_i^\circ(x+\lambda)/\partial\lambda = \partial B_i^\circ(x+\lambda)/\partial x$$

we arrive at the following condition for the shift parameter λ:

$$\sum_{i=1}^{m} x_i \int dx \, [\, g_i(x) - g_i^\circ(x+\lambda)\,] \, \partial B_i^\circ(x+\lambda)/\partial x = 0 \qquad i=1,..m \qquad (3.6)$$

It should be noted that the HNC approximation for the density profiles (i.e. $B_i(x)=0$ without any additional statement about the bulk $B_{ij}(r)$'s) is obtained also from Wertheim's equation [22] : For a one component system

$$k_B T \nabla_r \log \rho(\underset{\sim}{r}) = -\nabla_r v_{ext}(\underset{\sim}{r}) + k_B T \int d\underset{\sim}{r}' c(\underset{\sim}{r},\underset{\sim}{r}') \, \nabla_r[\rho(\underset{\sim}{r}') - \rho] \qquad (3.7)$$

under the assumption

$$c(\underset{\sim}{r},\underset{\sim}{r}') = c_{Bulk}(|\underset{\sim}{r}-\underset{\sim}{r}'|) \qquad (3.8)$$

Employing the method of Carnie et al [23], we derive from (3.1) and (3.5) the following sum rule

$$\sum_{i=1}^{m} x_i g_i(R_i) + \beta \left(\sum_i x_i Q_i\right) \Psi(x=0) = \beta E_0^2/8\pi\rho + 1/2[1+\beta(\partial P/\partial\rho)_T]_{Bulk}$$
$$+ \sum_{i=1}^{m} x_i \int_0^\infty dx \, g_i(x) \, \beta \, \partial\phi_i^{SR}(x)/\partial x + \sum_{i=1}^{m} x_i \int dx \, g_i(x) \, \partial B_i(x)/\partial x \qquad (3.9)$$

If the exact bulk direct correlation functions (dcf) and the exact bridge functions $B_i(x)$ are employed, then eq.(3.9) is exact. It should be compared to the following exact relation that does not involve the bridge functions explicitly [2,24,25]

$$\sum_{i=1}^{m} x_i g_i(R_i) + \beta \left(\sum_{i=1}^{m} x_i Q_i\right) \Psi(x=0) = \beta E_0^2/8\pi\rho + \beta(P/\rho)_{Bulk}$$

$$+ \sum_{i=1}^{m} x_i \int dx\, g_i(x)\, \beta\, \partial\phi_i^{SR}(x)/\partial x \tag{3.10}$$

comparing these equations we find the following bridge function sum rule for the density profile

$$\sum_{i=1}^{m} x_i \int dx\, g_i(x)\, \partial B_i(x)/\partial x = \beta(P/\rho)_{Bulk} - 1/2[1+\beta(\partial P/\partial\rho)_T]_{Bulk} \tag{3.11}$$

When approximate bridge functions e.g $B_i^{\circ}(x)$ and /or approximate bulk dcf (c (r)) are used, then eq. (3.9) is still valid provided that the bulk inverse compressibility

$$\beta(\partial P/\partial\rho)_T$$

is taken from the compressibility equation of state which corresponds to the bulk dcf's that are employed. When $B_i(x)=0$ then we recover the more familiar HNC sum rule [23]. In the case of the mean spherical approximation (MSA) the closure for the dcf is

$$c_i(x) = -\phi_i(x)\ ,\quad x \geq R_i \tag{3.12}$$

for which we obtain from (2.11)

$$g_i(x)\ \partial B_i(x)/\partial x\big|_{MSA} = g_i(x)\partial g_i(x)/\partial x - \partial g_i(x)/\partial x \tag{3.13}$$

and from (3.9)

$$1/2\sum_{i=1}^{m} x_i g_i^2(R_i) + \beta\left(\sum_{i=1}^{m} x_i Q_i\right) \Psi(x=0) = \beta E_0^2/8\pi\rho + 1/2[\beta(\partial P/\partial\rho)_T]_{BULK}$$

$$+\sum_{i=1}^{m} x_i \int dx\ g_i(x)\ \beta\ \partial\phi_i^{SR}(x)/\partial x \tag{3.14}$$

Despite the extensive work on the MSA for density profiles [2,11,26], this general MSA sum rule has not, to our knowledge been published in the literature. This MSA sum rule, as well as the general sum rule (3.9), are very useful in understanding the results of the different approximations.

Returning to the MHNC approximation with the hard sphere reference bridge functions $B_i^\circ(x+\lambda)$, we write, from (3.6)

$$\sum_{i=1}^{m} x_i \int dx\ g_i(x)\ \partial B_i^\circ(x+\lambda)/\partial x = \sum_{i=1}^{m} x_i \int_0^\infty dx\ g_i^\circ(x)\ \partial B_i^\circ(x)/\partial x$$

$$-\sum_{i=1}^{m} x_i \int_0^\lambda dx\ g_i^\circ(x)\ \partial B_i^\circ(x)/\partial x \tag{3.15}$$

Using (3.11) applied to the reference system, and also (3.9), we obtain the following MHNC result for the density profiles:

$$\sum_{i=1}^{m} x_i g_i(R_i) + ß \left(\sum_{i=1}^{m} x_i Q_i\right) \Psi(x=0) = ßE_o^2/8\pi\rho$$

$$+\sum_{i=1}^{m} x_i \int dx\; g_i(x)\; ß\; \partial\phi_i^{SR}(x)/\partial x + 1/2[1+ß(\partial P/\partial\rho)_T]_{\substack{Bulk\\MHNC}} + [ß(P/\rho)]^{\circ}_{Bulk}$$

$$-1/2[1+ß(\partial P/\partial\rho)_T]^{\circ}_{Bulk} - \sum_{i=1}^{m} x_i \int_0^{\lambda} dx\; g_i^{\circ}(x)\; ß\; \partial B_i^{\circ}(x)/\partial x \qquad (3.16)$$

where , for all practical purposes we may ignore the last term (i.e. $\lambda \leq R_i$ of the right hand side [27].

Comparing (3.16) with (3.9) and (3.10), we find that in all cases when the bulk dcf's and equation of state are given correctly by the MHNC (as it is the case for simple, one component fluids),a criteria for the performance of the accuracy of the MHNC for the density profile of the inhomogeneous case is provided by the validity of the following bulk relation (the 'bridge sum rule')

$$[ß(P/\rho)] - 1/2[1+ß(\partial P/\partial\rho)_T] = [ß(P/\rho)]^{\circ} - 1/2[1+ß(\partial P/\partial\rho)_T]^{\circ} \qquad (3.17)$$

Denoting by $f(\rho,T) = ßF^{ex}/N$ the excess free energy per particle then we may re-write (3.17) as

$$-\rho^2/2\; \partial^2 f(\rho,T)/\partial\rho^2|_T = -\rho^2/2\; \partial^2 f^{\circ}(\rho,T)/\partial\rho^2|_T \qquad (3.18)$$

Thus, an optimized MHNC map (i.e.$R^{\circ}(ß,\rho)$) of the system on the reference system, such that the optimized bridge parameters obtained

from (2.9) reproduce accurately the structure functions of the system, will perform as well for the density profiles, provided that the optimized reference bulk system and the given bulk system have the same second partial density derivatives.This result is an unexpected type of correlation between the bulk bridge parameters.

IV-Test of the Bridge Sum Rule:Universality of the Wall-Particle Bridge Functions

For bulk fluids in three dimensions the exact bridge functions are not known:However the universality hypothesis can be tested very effectively:The bridge functions obtained from the Percus-Yevick theory for hard spheres reproduces the structural correlation functions obtained by computer simulation of a large variety of cases, with quite disparate interaction potentials, from hard spheres to charged plasmas [1,12-21].The corresponding MHNC calculations employ the PY-hard sphere bridge functions with a single parameter η (which is the hard sphere packing fraction in the PY approximation).As a result, we have available the values of η (ρ,T) for the set of potentials for which detailed MHNC calculations have been performed.These include the hard spheres, Lennard-Jones (LJ 12-6) ,r^{-12},r^{-6} and r^{-1}(the OCP) potentials[1,6,18,19]. As already discussed in detail elsewhere [13] when the bridge parameter is expresed in terms of the entropy $S=-S^{ex}/Nk$,then $\eta(S)$ forms a universal line, independent of the potential (fig 1 of ref: 13).This represents a graphic demonstration of the accuracy of the variational thermodynamic perturbation theory.The result (3.17) has not been anticipated.

The test of the validity of (3.17) and of the universality of the bridge functions for the density profiles can be performed together by examining the universality of the bulk bridge parameter n ,when expressed in terms of

$$F=-[\beta(P/\rho)]-1/2[1+\beta(\partial P/\partial\rho)_T]$$

$$= \rho^2/2 \; \partial^2 f(\rho,T)/\partial\rho^2 \qquad (4.1)$$

for different potentials. It is to be emphasized that this broad interpretation of the universality η (F) requires only that a set of bridge functions from which this relation is obtained does accurately reproduce the bulk pair correlation functions. In figure 1 we plot the results for η (F) for different potentials in the entire fluid range, $\eta<0.45$. Indeed, the universality is satisfied to a ramarkable degree. Better, in fact than that of η(S). The hard sphere line in figure 1 is actually obtained from simple analytic expressions. For hard spheres, using the packing fraction $\xi=\pi/6\,\rho d^3$ (where d is the hard sphere diameter), we use the Carnahan-Starling equation of state [29] to get

$$F_{\text{hard spheres}}=[5\xi^2-2\xi^3]/[1-\xi]^4 \qquad (4.2)$$

This expression provides also an excellent fit for the MHNC calculations of Tsai [18], who obtained the representation for the parameter η

$$\eta = (0.982913-0.02271\xi+0.02449\xi^2)^3 \qquad (4.3)$$

The universal behaviour of η(S) and η(F) for simple one component fluids suggests a new interesting possibility to correlate the bulk properties of simple classical fluids using a relation of the type

$$S(F)= \text{universal function} \qquad (4.4)$$

V-An Example: The one Component Plasma in Contact with an Impenetrable Wall

Monte Carlo (MC) simulations of the surface properties of the OCP were performed by Badiali et al [5]. These authors present the results for an near an impenetrable hard wall for five values of the plasma coupling parameter

$$\Gamma = \beta Q^2/a_{ws} = 1, 10, 20, 30, 70 \qquad a_{ws} = [3/4\pi\rho]^{1/3}$$

In addition to the MC result they also present results for the HNC closure for the density profile using the MC results for the bulk dcf, and results for the MSA for the density profile [26] using the soft MSA [30,17] bulk dcf's. We will refer to those results as MC/MC, HNC/MC and MSA/SMSA.

For the case at hand, $\phi^{SR}(x)=0, E_o=0, R=0$, and in the notations of ref [5], $\beta QU(0) = -\beta ze\Delta\Psi$. Denoting

$\Delta\Psi = \beta ze\Delta\Psi - g(0)$ in general and $\Delta\Psi = \beta ze\Delta\Psi - g^2(0)/2$ for the MSA, we obtain the following results for the different theories

$$\Delta\Psi = 1/2[1+\beta(\partial P/\partial\rho)_T]_{\substack{bulk\\MC}} \quad \text{for HNC/MC}$$

$$\Delta\Psi = 1/2[1+\beta(\partial P/\partial\rho)_T]_{\substack{bulk\\SMSA}} \quad \text{for MSA/SMSA}$$

$$\Delta\Psi = 1/2[1+\beta(\partial P/\partial\rho)_T]_{\substack{bulk\\HNC}} \quad \text{for HNC/HNC}$$

$$\Delta\Psi = \beta(P/\rho)]_{\substack{bulk\\MC}} \quad \text{for MC/MC}$$

$$\Delta\Psi = \beta(P/\rho)]_{\substack{bulk\\MHNC}} - (F-F^\circ) \quad \text{for MHNC/MHNC}$$

(5.1)

Recall, that, essentially, MHNC/MHNC$\simeq$MHNC/MC and that the OCP results give $\eta(\Gamma=1)\sim 0.1, \eta(\Gamma=70)\sim 0.38$ (see fig.1 in ref 6).Using fig.1 with $\Delta F = F - F^{\circ}$ given in relation to the hard sphere line we find

for $\Gamma = 1$, 10 , 20 , 30 , 70

we find $\Delta F = 0$, 0.20, 0.25 , 0.15 , -0.25 respectively.Recall also that for the bulk,HNC~MC for $\Gamma=1$, while [17,31], HNC~SMSA for $\Gamma \gtrsim 10$. The reults of the different theories for $\Delta \Psi$ are given in table 1.Note the high accuracy obtained by the MHNC/MHNC when compared to the MC/MC. Note also that without succeeding to reproduce the pronounced structures of the MC/MC density profiles,all the theories of the type X/HNC or X/SMSA with X=HNC or MSA will give, for large plasma parameter Γ , much better results for the total potential drop $\Delta \Psi$ than the corresponding X/MC.This is a negative feedback artifact of the thermodynamic inconsistency of the HNC and SMSA results for the bulk OCP, by which they give

$1/2\beta\ (\partial P/\partial \rho)_T \sim 0.3\ \Gamma$,wich happens to agree with $\beta\ (P/\rho) \sim 0.3\ \Gamma$ This situation is very similar to what happens in the bulk OCP where both the HNC and the SMSA give very good results for the potential energy despite ($\Leftrightarrow \Delta\Psi$) the fact that the corresponding pair correlation functions are far from reproducing the MC results. The MHNC/MHNC results satisfy a stringent moment test, i.e.(3.6) which as in the bulk case also assures the validityof the $\Delta \Psi$ ($\Leftrightarrow$ potential energy) test in table 1.

VI-Construction of the Bridge Functions for the Density Profiles

Despite the fact that we have used the PY hard sphere representation for the bulk bridge functions in constructing the MHNC scheme for the inhomogeneous problem, the universality criteria for the bridge functions for the density profiles in the inhomogeneous fluid and eq. (3.17) are valid in all cases. The universality of n(F) tells us that there is a similarly universal representation of the bridge functions for the density profiles, but it does not necessarily imply that it can be obtained from the PY hard sphere density profiles. Yet, the general behaviour of the universal bridge functions for the density profiles in the range z>0 is similar to that of the bulk fluid and may be inferred from the solution of the PY equation for hard spheres near a wall, which is, quite naturally, a good starting point.

The solution of the PY equation for a one component hard sphere system of bulk packing fraction n, near a hard wall yields [9]

$$c(z)=\begin{cases} -(1+2\eta)^2/(1-\eta)^4 & \text{for } z<-1/2 \\ [-(1+2\eta)^2+6\eta(1+\eta/2)(1+2\eta)(z+1/2)^2-2\eta(1+2\eta)^2(z+3/4)^3]/(1-\eta)^4 & \\ \qquad\qquad \text{for } -1/2<z<1/2 & \\ 0 \qquad\qquad \text{for } z>1/2 & \end{cases} \tag{6.1}$$

where z is is the distance to the wall and the hard core diameter d=2R is the unit of length. g(z) can be calculated from the planar OZ as described in [9]. By a method similar to that of the bulk case [1], the bridge functions for the density profiles are given by

$$B\ \ (z)=\begin{cases} -c(z)-1-\ln[-c(z)] & ,z<1/2 \\ g(z)-1-\ln[g(z)] & ,z>1/2 \end{cases} \qquad (6.2)$$

These functions are continuous, since as it is well known

$$c(1/2)=-g(1/2)=-(1+2\eta)/(1-\eta)^2 \qquad (6.3)$$

in agreement with (3.14) for hard spheres

$$1/2\ g^2(1/2)=1/2\beta(\partial P/\partial\rho)|_T\ =-1/2c(0)| \qquad (6.4)$$

The density profiles exhibit more pronounced structure than the bulk pair correlation functions, but the general shape of $B_{PYHS}(z)$ for $z\gtrsim 0$, is very similar to that of the bulk $B_{PYHS}(r)$ for $r>0$. Note however, that negative values of $g(z)$ occur for $\eta\gtrsim 0.45$, while negative values for the bulk $g(r)$ occur only for $\eta\gtrsim 0.63$. Bulk MHNC calculations, as well as the variational perturbation theory map the fluid range of simple fluids onto [13] $\eta(\rho,T)<.45$, with $\eta(\rho,T)\sim 0.45$ serving as a Lindemann type freezing rule. The singularity of the functions (6.2), associated with negative or zero values of $g(z)$, which limits their range to $\eta\lesssim 0.45$, may be more than accidental. Notwithstanding this speculative interpretation, one should be cautious in applying the bridge functions (6.2) for a fluid near its bulk freezing point. The overall general features regarding the application of the MHNC scheme to density profiles are similar to the bulk case. Accurate simulation data, when compared to MHNC

results will provide the ultimate test for the accuracy of the bridge functions.

VII-Conclusions

In this paper,devoted to the analysis of the density profile problem as the 'planar' limit of a bulk mixture in which one of the bulk particles increases in size to become the planar wall,we provided strong evidence for the universality of the bridge functions for the density profiles. Although we still have room for improvement of the parametric representation of the bridge functions, the resulting MHNC theory is likely to be as accurate as in the bulk case.A program for computing density profiles by means of the MHNC scheme is currently underway.

An attempt to implement the universality of the bridge functions for bulk uniform systems to the treatment of nonuniform fluids has already been made with considerable success [32].From the present analysis, it seems however that fruitful information, leading to a systematic improvement of the theory of nonumiform fluids, may be obtained by comparing the MHNC results for the density profiles to those obtained using the weighted density functional formalism [33].

Final test of the accuracy of this theory will be achieved by comparison to computer simulations.We hope to perform such a study in the future.

References

1) Y.Rosenfeld and N.W.Ashcroft,Phys.Revs. A20,1208,(1979).

2) L.Blum.J.Hernando and J.L.Lebowitz, J.Phys.Chem., 87,2825(1983).

3) See,for example the review by L.Blum,"The Electric Double Layer-a Comprehensive Approach",in Fluid Interfacial Phenomena,Edited by C.A.Croxton,J.Wiley & sons, New York, 1985.

4) See,for example the reviews by J.P.Hansen and M.Baus, Phys. Rep. 59,1 (1980);S.Ichimaru, Rev.Mod. Phys. 54, 1017 (1982).

5) J.P.Badali, M.L.Rosinberg, D.Levesque and J.J.Weis, J.Phys.C16,2183 (1983)

6) M.Hasegawa and M.Watanabe J.Phys.C18,2081 (1985), and references cited therein.

7) J.Goodisman and M.L.Rosinberg,J.Phys.C16,1143 (1983).

8) P.Ballone,G.Senatore and M.Tosi, Physics 119A,356 (1983).

9 a) D.Henderson,F.F.Abraham and J.A.Barker, Mol.Phys.31,1291 (1976).

b) J.K.Percus, J.Stat.Phys.15,423 (1976).

10) L.Blum and G.Stell,J.Stat.Phys.15,439 (1976).

11) D.Henderson and L.Blum,J.Chem.Phys.69,5441 (1978).

12) Y.Rosenfeld, J.de Physique,Paris),Colloq. 41, C-77 (1980),Phys. Revs.Lett.44,146 (1980).

13) Y.Rosenfeld,Phys. Revs. A29,2877 (1984).

14) Y.Rosenfeld,J.Stat. Phys. 42,437 (1986)

15) F.Lado, Phys. Lett. 89A,196 (1982).

16) F.Lado,S.M.Foiles and N.W.Ashcroft, Phys. Revs. A28,2374 (1983).

17) Y.Rosenfeld,J.Stat. Phys. 37,215 (1984).

18) J.S.Tsai, Ph.D.Dissertation, North Carolina State University, 1980 (unpublished).

19) F.J.Rogers,D.A.Young,H.E.DeWitt and M.Ross,Phys. Revs. A28,2890 (1983)

20) P.Ballone,G.Pastore and M.Tosi,J.Chem.Phys.81,3174 (1984),J.Wiecken J.Phys.C18,L717 (1985).

21) G.C.Aers and M.W.C.Dharma-Wardana,Phys. Revs. A29,2734(1984), C.Caccamo,G.Malescio and L.Reatto,J.Chem.Phys.81,4093(1984) D.J.Gonzalez,M.J.Grimson and M.Silbert, Mol.Phys.54,1047 (1985).

22) M.S.Wertheim, J.Chem.Phys. 65,2377 (1976).

23) S.L.Carnie, D.Y.Chan,D.J.Mitchell and B.W.Ninham, J.Chem.Phys. 74,1572 (1981).

24) D.Henderson, L.Blum and J.L.Lebowitz,J.Electroanal.Chem.102,315 (1979)

25) H.Totsuji,J.Chem.Phys. 75,871 (1981).

26) J.P.Badiali and M.L.Rosinberg,J.Chem.Phys. 76,3264 (1982).

27) λ is expected to be positive only for interactions ρ (x) which are strongly attractive near the wall.For repulsive potentials λ is expected to be negative.

28) As shown in ref 14 above, MHNC calculations employing the hard sphere bridge functions (based on simulations) are essentially equivalent to using the PY hard sphere functions.

29) N.F.Carnahan and k.E.Starling,J.Chem.Phys. 51,635 (1969).

30) M.J.Gillan, J.Phys.C7,L1 (1974);L.Blum and A.H.Narten, J.Chem.Phys. 56,5197 (1972),A.H.Narten, L.Blum and R.H.Fowler J.Chem.Phys. 60,378 (1974);Y.Rosenfeld and N.W.Ashcroft, Phys. Revs. A20,2162 (1979).

31) Y.Rosenfeld and N.W.Ashcroft, Phys. Revs.A20,2162 (1979).

32) R.M.Neiminen and N.W.Ashcroft, Phys. Revs.A24,560 (1981).

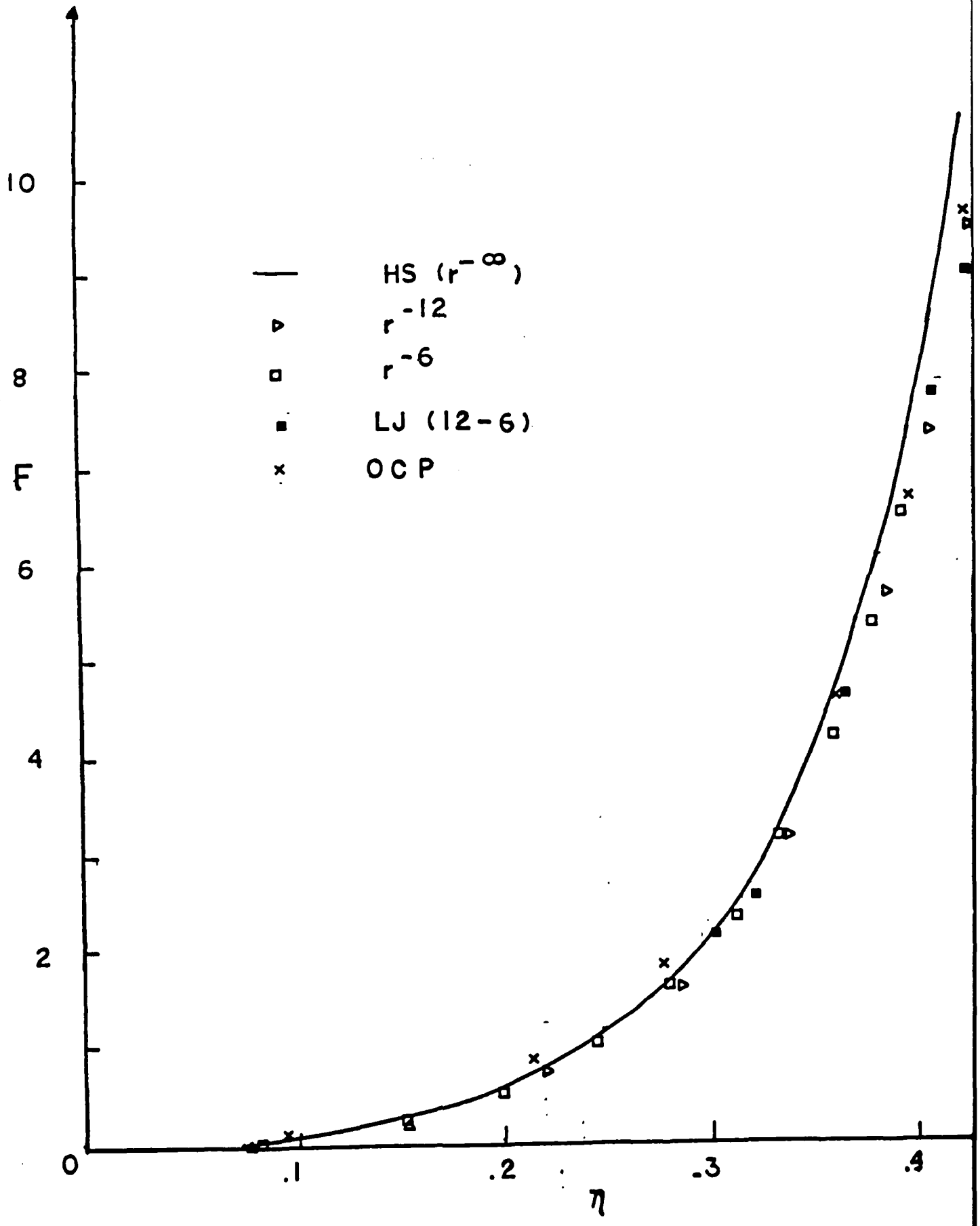
33) W.A.Curtin and N.W.Ashcroft, Phys. Revs.A32,2909 (1985).

Table 1 :Density profile sum rule for the OCP (see text, and also compare with table 2 in ref 5)

Γ					
	MC/MC	MHNC/MHNC	HNC/MC	MSA/MSA	HNC/HNC
1	0.81	0.81	0.87	0.44	0.86
10	-1.66	-1.86	-0.81	-1.40	-1.21
20	-4.56	-4.81	-2.75	-3.88	-3.81
30	-7.48	-7.33	-4.70	-7.20	
70	-19.28	-19.53	-12.59	-17.33	

Figure caption

Figure 1 : The bulk bridge function parameter n as a function of $F=1/2[1+\beta(\partial P/\partial\rho)_T] - \beta P/\rho$ for different potentials.The data is taken from references [1,13,14]. The Lennard -Jones results include data for both $T>T_c$ and $T<T_c$.


HS ($r^{-\infty}$)
r^{-12}
r^{-6}
LJ (12-6)
OCP
F
10
8
6
4
2
0
.1
.2
.3
.4
η

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