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The Self-Consistent Mean Spherical Approximation for the One-Component Plasma

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The consequences of choosing the adjustable hard-core diameter in the mean spherical approximation for the one-component plasma so as to achieve thermodynamic consistency between the energy and compressibility equations are investigated. Such a choice is found to be possible only for $\Gamma \gtrsim 8.5$ and, although the resulting correlation functions are discontinuous, the height of the main peak in the static structure factor is remarkably accurate. Two especially noteworthy aspects of the thermodynamic results are that the compressibility equation is much more accurate than in any previous approximation free of input from computer simulations and that the nonstatic part of the internal energy has a $\Gamma^{1/4}$ dependence in the strong coupling limit in agreement with Monte Carlo data.

KEY WORDS: Thermodynamic consistency; strongly coupled plasmas; mean spherical approximation.

1. INTRODUCTION

In many different contexts within the equilibrium statistical mechanics of classical fluids, self-consistency between the virial and compressibility equations of state has been found to be a very strong constraint in achieving accurate correlation functions from integral equation theories. In recent years, so-called self-consistent calculations have involved the solution of an integral equation with *at least two* free parameters $\mu_i(\rho, T)$, where ρ and T are, respectively, the density and temperature of the fluid. $\mu_i(\rho, T)$ may then be chosen to fix the pressure and compressibility (and possibly other quantities) at the values obtained from Monte Carlo (MC) or molecular

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dynamics simulations. Because this procedure requires the prior availability of simulation data for thermodynamic properties so that simulation data for the static structural functions will generally also be available, it is most useful when the self-consistent structural data are obtained in analytic (or at least near analytic) form. Calculations of this type are therefore usually based on variants of the mean spherical approximation (MSA) and examples of fluids which have been treated in this way are hard spheres (HS),[1] the restricted primitive model electrolyte,[2,3] and the one-component plasma (OCP).[4,5] A minor irritation of these calculations is that they should strictly be repeated if more reliable simulation data become available at a later date, but it should be emphasized that they all yield very accurate structural data.

The original idea of self-consistent integral equations[6] (which is used in the present paper) was, however, to solve an equation with a *single* free parameter $\mu(\rho, T)$ chosen to impose self-consistency without any input of simulation data. That is, the two equations of state were made identical but were not both made identical to some *a priori* expression. Clearly a self-consistent calculation of this type, even for just a single thermodynamic state, requires that results be obtained along a complete isotherm. This is also true for the self-consistent integral equation of Schneider *et al.*,[7] which, although containing no adjustable parameter, does involve an explicit density derivative. So far as is known to the present author, this equation has not been solved numerically for any classical fluid.

The earliest self-consistent integral equations were based on the Ornstein–Zernike equation with a closure relation intermediate between the hypernetted chain (HNC) and Percus–Yevick (PY) closures. The basic idea seems to have originated with Rowlinson,[6] who, however, only carried out calculations for the HS fluid at the level of expansion in virial coefficients. Numerical calculations for HS were carried out by Lado[8] using the same approximation as Rowlinson. Later, Hutchinson and Conkie[9] applied a different HNC–PY hybrid closure both to the HS fluid and to fluids interacting through inverse power potentials, especially the sixth and twelfth but not including the OCP. More recently, Rosenfeld and Ashcroft[10] proposed a modified HNC (MHNC) theory with which they were able, by a suitable choice of their free parameter η, to obtain good agreement with many simulation data for a wide range of fluids. Tsai[11] carried out proper self-consistent calculations with this MHNC scheme, but his results for HS and inverse power potentials do not significantly improve on those of Ref. 9.

The numerical computations involved in self-consistent theories are rather cumbersome: the virial pressure and the compressibility are both

calculated for a series of densities increasing stepwise from zero and the compressibility is integrated to yield a second pressure, the free parameter being chosen at each density to ensure self-consistency up to that density. It is therefore no accident that almost all fluids treated thus have thermodynamic properties depending on ρ and T only through a single combination of the two, since this permits a complete description of the fluid based on information along a single isotherm. Tsai's self-consistent MHNC calculations for the Lennard–Jones fluid along a subcritical isotherm[11] indicate a further difficulty: the compressibility cannot be integrated over a two-phase region. This problem was overcome (with some loss of numerical accuracy) by differentiating the virial pressure rather than integrating the compressibility. It is much simpler to use a local criterion for fixing η in the MHNC scheme and a method based on free energy minimization has recently been proposed by Lado.[12] Unfortunately, his compressibility results lack the accuracy of those of Ref. 10.

Although the parametrized closures discussed above do lead to an improvement over non-self-consistent results they appear somewhat *ad hoc* and not very physically based. In the MSA for soft-cored potentials, by contrast, there appears an adjustable parameter (the hard-core diameter σ, or equivalently the packing fraction $\eta = \frac{1}{6}\pi\rho\sigma^3$) which has a rather natural physical interpretation.[13] For most soft-cored potentials, fixing $\eta(\rho, T)$ to ensure self-consistency would again involve considerable computational effort but in the special case of the OCP the computation required is negligible due to the existence of the analytic solution of Palmer and Weeks.[14] Thus it is the purpose of this paper to present the self-consistent MSA (SCMSA) for the OCP with η as the single adjustable parameter and without input from simulations. Other criteria for choosing η in the MSA for OCP have been considered previously by Gillan[15] and MacGowan[16,17] and the present method will be compared to these.

2. STATEMENT OF THE PROBLEM

Three recent review articles[18,19,20] largely devoted to it give a clear indication of considerable interest in the OCP. The static properties of an OCP (point ions of charge Ze in a uniform neutralizing background) are entirely expressible in terms of the coupling constant $\Gamma = (Ze)^2/k_B Ta$ and the dimensionless length $x = r/a$ where $a = (3/4\pi\rho)^{1/3}$ is the ion-sphere radius. The starting point of the present investigations is the solution of the MSA for one-component charged spheres[14] which is directly applicable to the OCP. The notation adopted is that of Ref. 16 which is more suitable for describing the OCP than the notation of the original solution. The basic

equations of the MSA for OCP are

$$h(x) = -1, \qquad x < 2\eta^{1/3} \tag{1}$$

$$c(x) = -\Gamma/x, \qquad x > 2\eta^{1/3} \tag{2}$$

$$h(x) = c(x) + \frac{3}{4\pi}\int d^3x' c(|\mathbf{x} - \mathbf{x}'|)h(x') \tag{3}$$

where $h(x)$ and $c(x)$ are, respectively, the total and direct correlation functions, and the packing fraction η may be regarded as an arbitrary function of Γ. The solution of Eqs. (1)–(3) is

$$c(x) = \begin{cases} (2u - \alpha) + 3\eta^{2/3}D^2x + \frac{1}{2}\Gamma x^2 + \frac{1}{16}(4u - \alpha)x^3 + \frac{1}{160}\Gamma x^5, \\ \qquad\qquad\qquad\qquad\qquad\qquad x < 2\eta^{1/3} \\ -\Gamma/x, \qquad x > 2\eta^{1/3} \end{cases} \tag{4}$$

where

$$D = 1 + h(2\eta^{1/3} +) = \frac{1}{6\eta(1-\eta)^2}\left\{3\eta(\eta + 2) - R^2\right\} \tag{5}$$

$$u = \frac{3}{2}\Gamma\int_0^\infty xh(x)\,dx = \frac{1}{6}\left[\frac{R\lambda}{\eta^{2/3}} - \frac{(1 + \eta - \frac{1}{5}\eta^2)\lambda^2}{\eta^{1/3}}\right] \tag{6}$$

$$\alpha = 1 - 3\int_0^\infty x^2\left[c(x) + \frac{\Gamma}{x}\right]dx$$

$$= -\tfrac{1}{3}\eta^{2/3}(1 - \tfrac{2}{5}\eta)\lambda^2 - \tfrac{2}{3}\eta^{1/3}(1-\eta)^{-1}R\lambda - (1-\eta)^{-4}\left[R^2 - (2\eta + 1)^2\right] \tag{7}$$

$$\lambda = (3\Gamma)^{1/2} \tag{8}$$

$$R = (\eta + \tfrac{1}{2})\left\{\left[1 + \frac{(1-\eta)^3\eta^{1/3}}{(\eta + \frac{1}{2})^2}\lambda\right]^{1/2} - 1\right\} \tag{9}$$

It is clear from the first equalities of (6) and (7) that $u(\Gamma, \eta)$ and $\alpha(\Gamma, \eta)$ represent, respectively, the dimensionless excess internal energy per ion and the dimensionless inverse isothermal compressibility of the one-component charged sphere fluid. The corresponding properties of the OCP are

$$u^0(\Gamma) = u(\Gamma, \eta(\Gamma)) \tag{10}$$

$$\alpha^0(\Gamma) = \alpha(\Gamma, \eta(\Gamma)) \tag{11}$$

and the self-consistency condition to be imposed is

$$\alpha^0(\Gamma) = 1 + \frac{1}{3}u^0(\Gamma) + \frac{1}{9}\Gamma\frac{du^0}{d\Gamma} \tag{12}$$

Equation (12) is equivalent to virial-compressibility consistency since, for the OCP, the virial equation of state is

$$\frac{p^0}{\rho k_B T} - 1 = \frac{1}{3}u^0 \tag{13}$$

To be more explicit, the task of solving the MSA for OCP self-consistently is effectively that of solving the highly nonlinear ordinary differential equation

$$\left[\frac{1}{9}\Gamma\left(\frac{\partial u}{\partial \eta}\right)_\Gamma\right]\frac{d\eta}{d\Gamma} = \alpha - 1 - \frac{1}{3}u - \frac{1}{9}\Gamma\left(\frac{\partial u}{\partial \Gamma}\right)_\eta \tag{14}$$

for $\eta(\Gamma)$, where $u(\Gamma,\eta)$ and $\alpha(\Gamma,\eta)$ are given by (6) and (7), respectively. When considering suitable boundary conditions for (14) it is natural to impose on any solution the reasonable physical requirement

$$D \geqslant 0 \tag{15}$$

which is equivalent[21,16] to

$$(\partial u/\partial \eta)_\Gamma \leqslant 0 \tag{16}$$

In terms of $\eta(\Gamma)$ the above conditions may be stated as

$$\eta_C(\Gamma) \leqslant \eta(\Gamma) < 1 \tag{17}$$

where $\eta_C(\Gamma)$ is the defining function of Gillan's continuous MSA (CMSA).[15] Equation (17) is a tighter restriction on $\eta(\Gamma)$ than $0 < \eta(\Gamma) < 1$ which is necessary for the MSA to have real solutions.

The most interesting boundary condition to impose on (14) is $\eta(\Gamma)\to 1$ as $\Gamma\to\infty$, which is dictated by (17) since $\eta_C(\Gamma)\to 1$ as $\Gamma\to\infty$. This boundary condition will be discussed in Section 3 with the assumption that, locally, the solution has a power law behavior, but the question of uniqueness of solutions will not be tackled. There follows first a brief digression to consider the possibility of satisfying the alternative boundary condition $\eta(\Gamma)\to 0$ as $\Gamma\to 0$ which would give the ideal gas limit.

In seeking a SCMSA in the limit $\Gamma\to 0$ it should first be noticed that $u\to 0$ as $\Gamma\to 0$ irrespective of η $(0 < \eta < 1)$. Thus $\alpha\to 1$ as $\Gamma\to 0$ is a requirement for self-consistency and it is only satisfied if $\eta\to 0$ as $\Gamma\to 0$.

Then the low-order expansions

$$u \sim -3\Gamma\eta^{2/3} - (\sqrt{3}/2)\Gamma^{3/2} \tag{18}^2$$

and

$$\alpha - 1 \sim -6\Gamma\eta^{2/3} + 8\eta \tag{19}$$

are easily obtained and (14) becomes, in the weak coupling limit,

$$\left[\frac{1}{9}\Gamma\left(\frac{\partial u}{\partial \eta}\right)_{\Gamma\to 0}\right]\frac{d\eta}{d\Gamma}\bigg|_{\Gamma\to 0} = 8\eta - \frac{14}{3}\eta^{2/3}\Gamma + \frac{\sqrt{3}}{4}\Gamma^{3/2} \tag{20}$$

Since η dominates $\eta^{2/3}\Gamma$ provided η vanishes more slowly than Γ^3 and $\Gamma^{3/2}$ dominates $\eta^{2/3}\Gamma$ provided η vanishes faster than $\Gamma^{3/4}$, the right-hand side of (20) is always positive as $\Gamma \to 0$. The left-hand side, however, is negative [in view of condition (16) and the positivity of η] and so (20) cannot be satisfied. The resulting conclusion that there is no SCMSA for OCP in the weak-coupling limit appears to be confirmed by the failure to obtain numerical self-consistent solutions for $\Gamma \lesssim 8.5$ which will be reported in Section 4.

3. THE STRONG COUPLING LIMIT

As has been explained above, the appropriate boundary condition for (14) as $\Gamma \to \infty$ is $\eta(\Gamma) \to 1$ and it is therefore convenient to work in terms of the variable $\epsilon = 1 - \eta$. Assuming only that $\epsilon(\Gamma) \to 0$ as $\Gamma \to \infty$ yields the ion-sphere result[20]

$$u^0 \sim -\tfrac{9}{10}\Gamma, \qquad \Gamma \to \infty \tag{21}$$

Clearly, from (21) and (12), the first requirement for a SCMSA in the strong coupling limit is $\alpha^0 \sim -\frac{2}{5}\Gamma$. Supposing now that $\epsilon \propto \Gamma^{-q}$ $(q > 0)$ as $\Gamma \to \infty$, the expansion of R depends strongly on whether $q > 1/6$ or $q < 1/6$. If $0 < q < 1/6$, however, it is found that the dominant term in α^0 obtained from Eq. (7) is $-\frac{3}{5}\Gamma$. For $q = 1/6$, R tends to a constant value as $\Gamma \to \infty$ and the conclusion reached for $0 < q < 1/6$ remains true. Gillan's CMSA furnishes a particular example of $q = 1/6$[22] for which the thermodynamic inconsistency in the strong coupling limit was earlier demonstrated by Rosenfeld and Ashcroft.[13]

From the above considerations it is certainly justified in seeking a SCMSA at large Γ to restrict attention to $q > 1/6$ in which case R can be

[2] Equation (18) shows that any $\eta(\Gamma)$ which vanishes faster than $\Gamma^{3/4}$ as $\Gamma \to 0$ yields the exact linear Debye–Hückel limiting result for u^0. A particular example of this was shown previously by Palmer[21] for Gillan's choice $\eta_C(\Gamma)$, when $\eta \sim \frac{1}{8}\Gamma^3$ in the limit $\Gamma \to 0$.

expanded in powers of ϵ and $\epsilon^3\lambda$ leading after tedious algebra to

$$\begin{aligned} u = &-\frac{3}{10}\lambda^2 + \frac{1}{27}\lambda^2\epsilon^3 + \frac{1}{27}\lambda^2\epsilon^4 + \frac{13}{405}\lambda^2\epsilon^5 \cdots \\ &-\frac{1}{162}\lambda^3\epsilon^6 - \frac{1}{81}\lambda^3\epsilon^7 \cdots \\ &+\frac{1}{729}\lambda^4\epsilon^9 \cdots \\ &+ \cdots \end{aligned} \tag{22}$$

$$\begin{aligned} \alpha = &\, 9\epsilon^{-4} - 12\epsilon^{-3} + 4\epsilon^{-2} \\ &-\frac{1}{5}\lambda^2 - \frac{2}{9}\lambda^2\epsilon^2 - \frac{4}{81}\lambda^2\epsilon^3 + \frac{88}{3645}\lambda^2\epsilon^5 \cdots \\ &+\frac{4}{81}\lambda^3\epsilon^5 + \frac{16}{243}\lambda^3\epsilon^6 + \frac{44}{729}\lambda^3\epsilon^7 \cdots \\ &-\frac{1}{81}\lambda^4\epsilon^8 - \frac{64}{2187}\lambda^4\epsilon^9 \cdots \\ &+\frac{8}{2187}\lambda^5\epsilon^{11} \cdots \\ &+ \cdots \end{aligned} \tag{23}$$

Clearly the two terms $9\epsilon^{-4}$ and $-\frac{1}{5}\lambda^2$ $(= -\frac{3}{5}\Gamma)$ in equation (23) are both potentially dominant. The condition for lowest order self-consistency is

$$-\tfrac{3}{5}\Gamma + 9\epsilon^{-4} = -\tfrac{2}{5}\Gamma$$

Hence, to lowest order,

$$\epsilon \sim (45/\Gamma)^{1/4} = \theta \tag{24}$$

If $q > 1/4$ the static term would no longer dominate α^0 and it has already been seen in Eq. (21) that the static term always dominates u^0 independently of the value of q. If, on the other hand, $1/6 < q < 1/4$ then, as for $q \leqslant 1/6$, $\alpha^0 \sim -\frac{3}{5}\Gamma$. Thus $q = 1/4$ is the only value which can lead to self-consistency to lowest order. It may be remarked at this point that the discontinuous MSA (DMSA, approximation IV of Ref. 16) also gave $\epsilon \propto \Gamma^{-1/4}$ as $\Gamma \to \infty$ but with a different proportionality coefficient such that $\alpha^0 \sim -\frac{1}{10}\Gamma$.

In order to go beyond the lowest order result, ϵ is expanded in powers of θ:

$$\epsilon = \sum_{\nu=1}^{\infty} b_\nu \theta^\nu, \qquad b_1 = 1 \tag{25}$$

The lowest-order ϵ is sufficient to give u^0 to $O(\Gamma^{1/4})$ but only gives α^0 consistent with this u^0 to $O(\Gamma)$ and so b_2, b_3, b_4 must all be fixed suitably to obtain α^0 to $O(\Gamma^{1/4})$. Then u^0 will be determined to $O(\Gamma^{-1/2})$ and by fixing b_5, b_6, b_7 α^0 may be made consistent with u^0 to that order. Proceeding in this way, a self-consistent strong coupling expansion of the MSA for OCP can in principle be carried out to arbitrarily high order in θ.

It should be noticed, however, that the first few b_ν obtained in this way are

$$b_2 = -\tfrac{1}{3}$$

$$b_3 = -\tfrac{7}{9}$$

$$b_4 = \frac{5\sqrt{15}}{9} + \frac{1135}{1296}$$

so that

$$\epsilon = 2.59002\Gamma^{-1/4} - 2.23607\Gamma^{-1/2} - 13.5134\Gamma^{-3/4} + 136.234\Gamma^{-1} \cdots \quad (26)$$

$$u^0 = -\frac{9}{10}\Gamma + 5\left(\frac{\Gamma}{45}\right)^{1/4} - \frac{5}{2}\sqrt{15} + \frac{38}{3}\left(\frac{45}{\Gamma}\right)^{1/4} \cdots \quad (27)$$

$$\alpha^0 = -\frac{2}{5}\Gamma + \frac{65}{36}\left(\frac{\Gamma}{45}\right)^{1/4} - \left(\frac{5}{6}\sqrt{15} - 1\right) + \frac{209}{54}\left(\frac{45}{\Gamma}\right)^{1/4} \cdots \quad (28)$$

Since the coefficients in these asymptotic series are rapidly increasing it may be expected that the series will not be very useful for $\Gamma \lesssim 170$ (in the physical fluid phase of the OCP). This is in contrast to the series for $\epsilon(\Gamma)$ as $\Gamma \to \infty$ in the CMSA[22] and DMSA.[16,17] In the DMSA, for example, the strong coupling expansion agrees remarkably well with the numerical results down to $\Gamma \simeq 70$.[17] In spite of the rapidly increasing coefficients in the present case, the preceding considerations indicate the possibility of a SCMSA for the strongly coupled OCP and, as will be mentioned below, its numerical results are actually well fitted for $80 \leqslant \Gamma \leqslant 170$ by the functional form

$$u^0 = A\Gamma + B\Gamma^y + C \quad (29)$$

with $y = 1/4$, which was chosen on the basis of the asymptotic result (27).

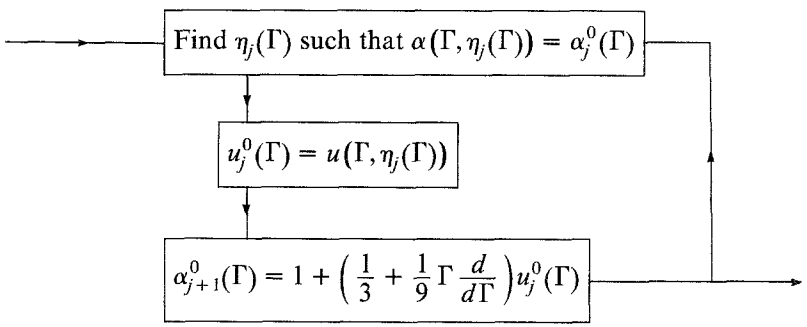
In many different approximations for the OCP it has been found that the nonstatic or thermal part of u^0 is proportional to Γ^y $(0 < y < 1)$ for large Γ in the fluid phase. The nonlinear least-squares fits of DeWitt[23] based on Eq. (29) gave $y \simeq 1/4$ for the MC data of Hansen[24] but $y = 1/2$ for the CMSA results[15] and also, with an extra term proportional to $\ln\Gamma$ added to (29), for the HNC results.[25] The later MC data of Slattery *et al.*[26] were accurately represented by (29) with $y = 1/4$ and an extra term

proportional to $\Gamma^{-1/4}$, but this was a linear least-squares fit *assuming* $y = 1/4$. The most recent MC data of Slattery *et al.*[27] lead to the less definite conclusion[28] $0.25 \lesssim y \lesssim 0.3$. Analytically determined values of y are available from several theoretical approximations.[22,29,16] Since these are conveniently summarized in Ref. 16 they will not be discussed in detail here and it is sufficient to recall that the only values of y obtained are $1/4$, $2/5$, and $1/2$. Thus, although the value of $y = 1/4$ is indicated with less certainty by the latest simulation results than by the previous results, it can still be stated that, of all the simple theoretical approaches to the OCP, only those yielding $y = 1/4$ are consistent with the most recent MC data.

The only approximations for which $y = 1/4$ are the present SCMSA, the DMSA, and the hard-sphere variational approximation (HSVA) of DeWitt and Rosenfeld.[29] Both HSVA and DMSA yield the same coefficient of $\Gamma^{1/4}$ which is rather close to the value obtained by fitting MC data but the corresponding SCMSA coefficient is not so close to the MC value. On the other hand, the ability of HSVA and DMSA to give $y = 1/4$ depends crucially on the use of a particular approximate expression, obtained through the PY virial equation, for the excess entropy of the HS fluid, whereas SCMSA is based on the exact requirement of thermodynamic consistency.

4. NUMERICAL RESULTS AND CONCLUSIONS

The iterative procedure used to obtain numerical solutions for the SCMSA is as follows:



The convergence criterion used was $|\alpha_{j+1}^0(\Gamma) - \alpha_j^0(\Gamma)| \leqslant 10^{-7}$ for all $\Gamma \gtrsim 9$ and by taking the initial input $\alpha_1^0(\Gamma)$ obtained through Eq. (12) from a MC fit for $u^0(\Gamma)$[26] the required number of iterations was kept down to around six. [It should be emphasized that, although using MC data as initial input speeds convergence, the final results after iteration are quite independent of

any input from simulations. This was checked by using several different expressions for $\alpha_1^0(\Gamma)$.] Convergence was achieved with greater difficulty for $8.5 \lesssim \Gamma \lesssim 9$, using a simple mixing scheme, but no self-consistent solution could be obtained for $\Gamma \lesssim 8.5$.

The differentiation step in the iteration scheme was carried out using a five-point finite-difference formula, and varying the Γ mesh spacing from 0.1 to 0.5 had no effect on the numerical results obtained. The resultant function $\eta_{SC}(\Gamma)$ is plotted in Fig. 1, $\eta_C(\Gamma)$ and $\eta_D(\Gamma)$, the corresponding functions for CMSA and DMSA, respectively, being plotted also for

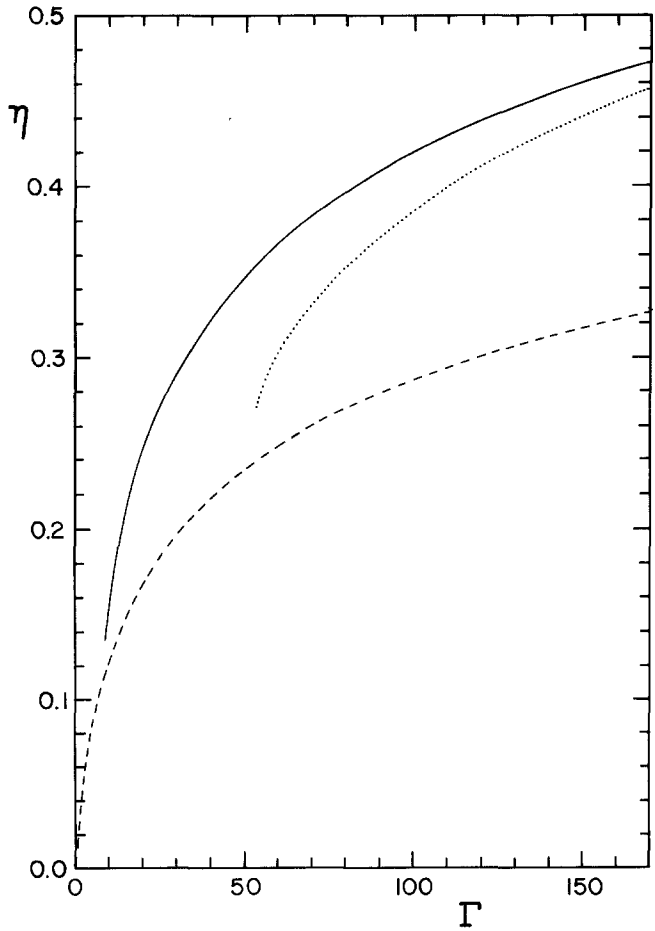


Fig. 1. The functions $\eta(\Gamma)$ defining the various MSAs for OCP: ——, SCMSA; - - -, CMSA; · · ·, DMSA.

comparison. It can be seen that self-consistency is achieved by increasing the excluded volume relative to the other MSAs but not by very much relative to the DMSA at high Γ. An alternative less accurate method of differentiation which is nevertheless of some interest was employed for $80 \leqslant \Gamma \leqslant 170$: the results for $u_j^0(\Gamma)$ were least-squares fitted by (29) with $y = 1/4$ (fixed on the basis of the $\Gamma \to \infty$ limit) and $\alpha_{j+1}^0(\Gamma)$ was obtained by analytic differentiation of this fit. Results found in this way were remarkably close to the more accurate results despite the doubts mentioned in Section 3 about the applicability of the strong coupling expansion to the physical fluid phase.

Tables I and II compare the OCP internal energies and compressibilities, respectively, for the different MSAs with the MC results of Slattery *et al.*,[26] α_{MC}^0 being obtained from u_{MC}^0 through Eq. (12). The SCMSA u^0 is consistently lower than u_{MC}^0 (the magnitude of u_{SCMSA}^0 is an overestimate) for all values of $\Gamma \geqslant 8.5$ but the discrepancy is never more than 1%. The self-consistent u^0 is more accurate than Gillan's value for $\Gamma \gtrsim 50$ and less accurate for $\Gamma \lesssim 50$. DMSA results for u^0 are generally the most accurate at all values of Γ where they exist. As was anticipated, the most dramatic consequence for the thermodynamic properties of imposing self-consistency on the MSA is the improvement in the compressibility, which is always within 1% of the MC value for $\Gamma > 10$ and is relatively even better at higher

Table I. Dimensionless Excess Internal Energy of the OCP

		$u^0 - u_{MC}^0$		
Γ	u_{MC}^0	SCMSA	CMSA	DMSA
10	− 7.99	− 0.08	− 0.06	—
20	− 16.67	− 0.12	0.00	—
30	− 25.44	− 0.14	0.06	—
40	− 34.25	− 0.16	0.13	—
50	− 43.09	− 0.17	0.19	—
60	− 51.96	− 0.18	0.25	0.14
70	− 60.83	− 0.19	0.30	0.11
80	− 69.71	− 0.20	0.35	0.08
90	− 78.61	− 0.20	0.40	0.06
100	− 87.51	− 0.21	0.45	0.04
110	− 96.41	− 0.22	0.50	0.02
120	− 105.32	− 0.23	0.54	0.00
130	− 114.23	− 0.24	0.59	− 0.03
140	− 123.15	− 0.25	0.63	− 0.05
150	− 132.07	− 0.26	0.67	− 0.07
160	− 140.99	− 0.27	0.71	− 0.09
170	− 149.92	− 0.28	0.75	− 0.12

Table II. Dimensionless Inverse Isothermal Compressibility of the OCP

	α^0			
Γ	MC	SCMSA	CMSA	DMSA
10	− 2.62	− 2.65	− 2.80	—
20	− 6.50	− 6.54	− 7.75	—
30	− 10.41	− 10.46	− 12.95	—
40	− 14.34	− 14.40	− 18.27	—
50	− 18.28	− 18.35	− 23.68	—
60	− 22.23	− 22.30	− 29.14	− 27.96
70	− 26.18	− 26.25	− 34.65	− 32.26
80	− 30.14	− 30.21	− 40.19	− 36.50
90	− 34.10	− 34.18	− 45.76	− 40.67
100	− 38.06	− 38.14	− 51.36	− 44.78
110	− 42.02	− 42.11	− 56.97	− 48.82
120	− 45.99	− 46.08	− 62.60	− 52.80
130	− 49.95	− 50.05	− 68.25	− 56.73
140	− 53.92	− 54.02	− 73.91	− 60.61
150	− 57.89	− 57.99	− 79.58	− 64.44
160	− 61.86	− 61.97	− 85.27	− 68.24
170	− 65.83	− 65.94	− 90.96	− 72.00

Γ. Thus $\alpha^0_{\mathrm{SCMSA}}$ is by far the most accurate OCP compressibility obtained from any approximation with no simulation input.

Figure 2 shows direct correlation functions from MSAs along with MC data[30] for $\Gamma = 40$, 100, and 160. SCMSA overestimates the magnitude of $c(0)$ but approaches the "exact" results away from $x = 0$ because $c_{\mathrm{SCMSA}}(x)$, unlike $c_{\mathrm{MC}}(x)$, has a nonzero derivative at $x = 0$. Although SCMSA clearly improves on CMSA, especially at high Γ, $c_{\mathrm{DMSA}}(x)$ appears to be the most accurate result at large Γ, mainly due to its short-range behavior. The fact that $\alpha^0_{\mathrm{SCMSA}}$ obtained from Eq. (7) is nevertheless much more accurate than the corresponding α^0_{DMSA} indicates that the region where $c(x) + \Gamma/x \to 0$ is much more important in determining α^0 than the region $x \to 0$.

Figure 3 shows static structure factors $S(k)$ determined from MC data[31] and from the SCMSA for several values of Γ. The SCMSA results are remarkably accurate for the height of the principal peak but this peak is always displaced to too large a value of k and the oscillations in the tail of $S(k)$ are both out of phase with the "exact" results and do not decay sufficiently rapidly. This last feature is an expected consequence of the discontinuity in $h(x)$. Figure 4 compares the static structure factors from the various MSAs at $\Gamma = 100$ and it is clear that SCMSA gives the best representation of the main peak. None of the simple MSAs gives a good fit

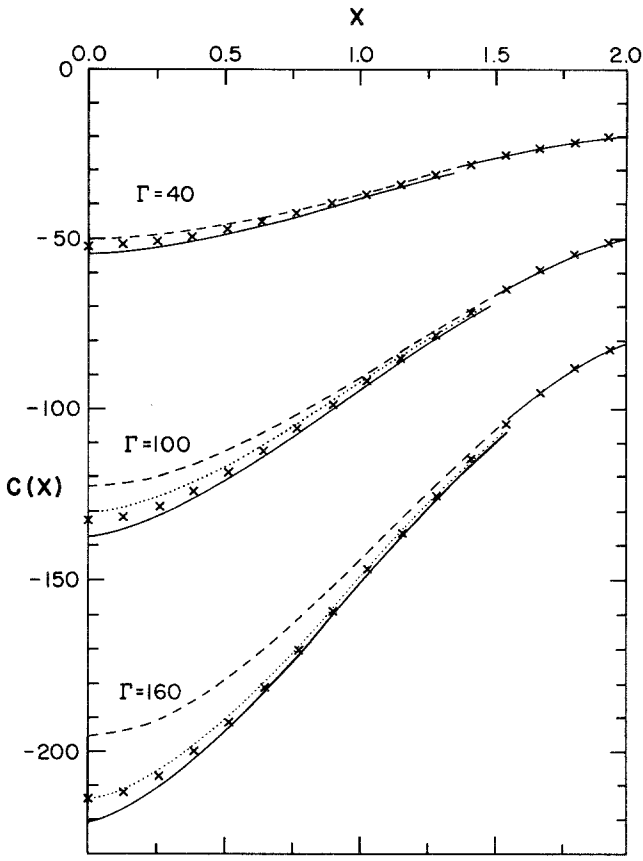


Fig. 2. OCP direct correlation functions: $\times\times\times$, MC, MSAs as for Fig. 1.

to the oscillatory tail of $S(k)$ and such a fit can only be obtained from more complicated approximations.[4,5]

In conclusion, it may be remarked that the surprising accuracy of Gillan's 1974 results[15] seems to have discouraged until recently attempts to obtain even better MSA results for the OCP. The present paper and Refs. 16 and 17 suggest a new attitude to such approximations: Gillan's choice should be regarded as a lower bound on possible choices of $\eta(\Gamma)$ since this is necessary for positivity of $1 + h(x)$. Continuity of $h(x)$ is of course desirable but not overwhelmingly so when there is in any case no chance of obtaining a smooth $h(x)$. Although the failure of the DMSA for $\Gamma \lesssim 53.6$ was a serious drawback, so that moderately successful attempts have been made to extend it to lower values of Γ,[17] the failure of SCMSA

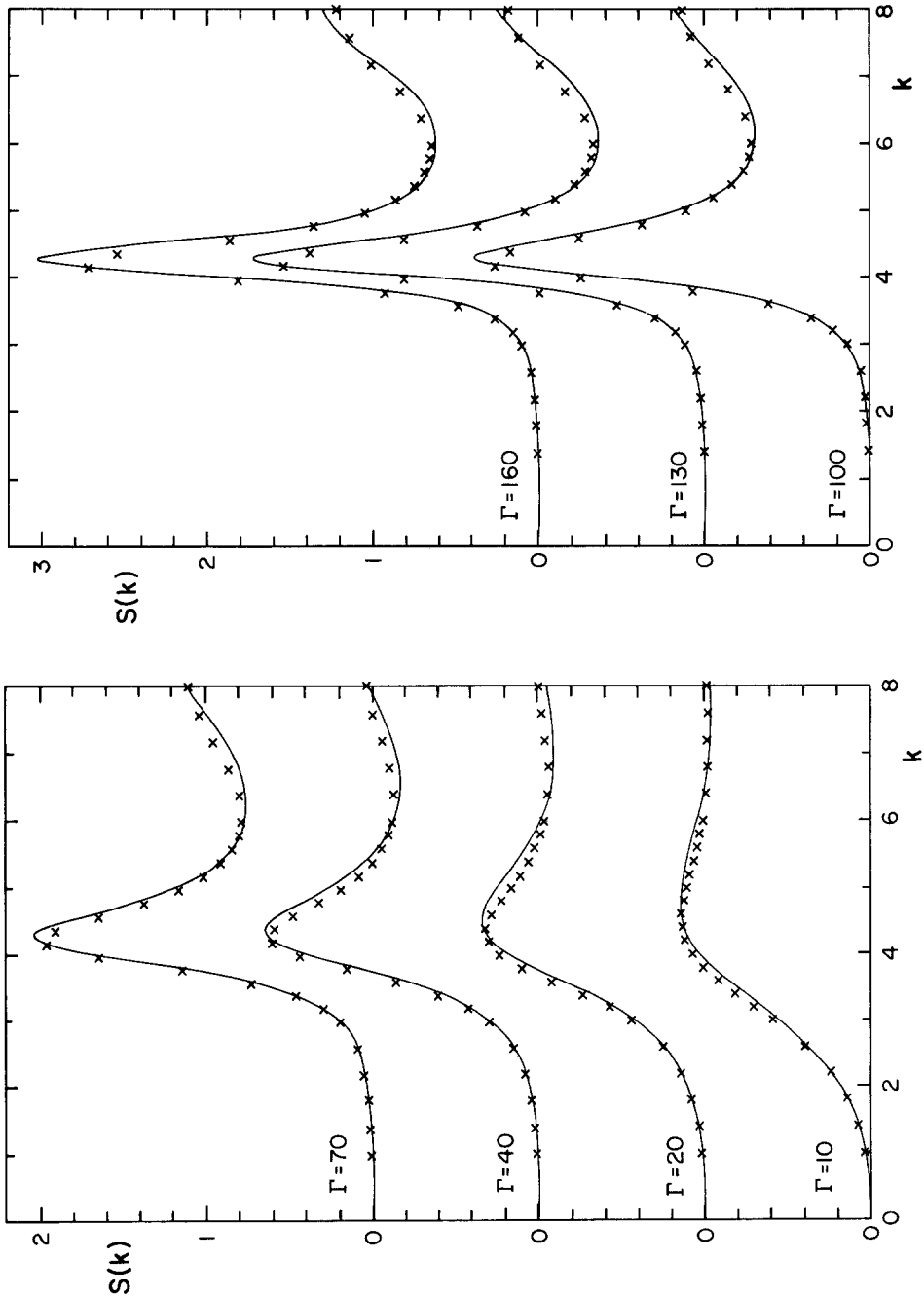


Fig. 3. OCP static structure factors (k in units of a^{-1}): $\times\times\times$, MC; ——, SCMSA.

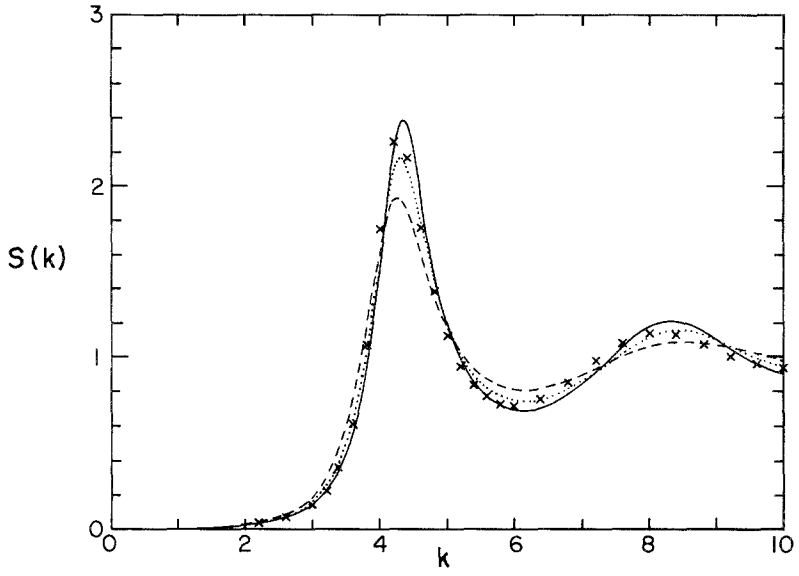


Fig. 4. The OCP static structure factor at $\Gamma = 100$: $\times\times\times$, MC; MSAs as for Fig. 1.

for $\Gamma \lesssim 8.5$ is quite unimportant since the hard-core aspect of the MSA is well known to be inaccurate at lower Γ.

The continuity condition on which the CMSA for OCP was originally based has been shown to be equivalent to $\partial u/\partial \eta = 0$,[21,32,16] but there is no clear physical significance for this thermodynamic statement. Both DMSA and SCMSA, however, are based on well-established thermodynamic criteria and they give superior results to CMSA for OCP at least at very strong coupling. It may therefore be expected that the use of thermodynamic rather than continuity conditions in MSAs for other soft-cored fluids will yield similarly improved results, albeit at some expense in the ease of obtaining them. In this connection it should be noticed that, since the SCMSA for OCP does not work right down to $\Gamma = 0$, the usual numerical procedure adopted in self-consistent calculations[8,9] of integrating the compressibility from $\rho = 0$ to obtain the compressibility equation of state would not have been possible here. The ease of the preceding computation is entirely due to the existence of the analytic expressions of Palmer and Weeks[14] and so SCMSAs for fluids other than the OCP may require much greater computational labor, especially if they also fail at $\rho = 0$.

Ionic mixtures in a uniform background perhaps represent the one class of fluids where a SCMSA might be calculated almost as easily as for

the OCP. The simplest such calculation would utilize the MSA solution of De Angelis *et al.* for a binary mixture of charged hard spheres with different charges but equal diameters.[33] A separate computation of the type described above would have to be carried out for each ratio of charges and each ratio of concentrations. On the basis of the OCP results, the strong coupling thermal energies could be expected to be quite accurate. These can have important implications for phase separation in certain astrophysical situations and no extensive MC data for ionic mixtures have been published.

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