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LETTER TO THE EDITOR

A semi-analytic theory for the static properties of a one-component plasma

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Abstract. A universal functional form is proposed for the direct correlation function of the one-component plasma. This form depends on only one scaling parameter which is determined from a novel hypernetted-chain compressibility equation through a single numerical integration. The results compare well with the numerical solutions of the hypernetted-chain integral equation as well as with recent Monte Carlo computations.

The study of the static and dynamic properties of charged fluids has recently become an active field of research in relation to astrophysics, thermonuclear fusion and chemical physics. Among the many modes studied so far, the one-component plasma (OCP) has emerged as a reference system playing a role similar to that of the hard-sphere system for uncharged fluids. The OCP consists of identical point charges with purely repulsive Coulomb interactions immersed in an inert and uniform neutralising background. The theoretical determination of the OCP statics is one of the many challenging problems raised by this relatively simple charged fluid. From the review article of De Witt (1978), we conclude that the results of Springer *et al* (1973) and Ng (1974), obtained on the basis of the numerical solutions of the hypernetted-chain (HNC) integral equation, provide, when compared with the Monte Carlo (MC) data of Hansen (1973), the most accurate description of the OCP statics presently available. It is our purpose here to present a simple model for the OCP statics which is partly analytical and which, with the aid of a single numerical quadrature for each value of Γ, yields results which compare favourably with the MC data and the numerical solutions of the HNC equations for all values of Γ belonging to the fluid phase ($0 \leqslant \Gamma \leqslant 155$). Here $\Gamma = \beta e^2/a$ is a dimensionless coupling parameter which characterises completely the excess thermodynamic properties of an OCP of temperature (in energy units) β^{-1} and of average number density $n = (\frac{4}{3}\pi a^3)^{-1}$, a being the mean ion-sphere radius, while e denotes the charge on each of the mobile particles.

We start by recalling that the MC data of Hansen (1973) have revealed that the direct correlation function $c(r)$ of the OCP exhibits little structure. For large r, $c(r)$ tends rapidly towards $-\beta V(r)$ whereas for small r it tends smoothly towards a finite value $c(0)$. Here $V(r)$ is the interaction potential, which for the OCP equals e^2/r, r being the interparticle

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distance. As a result of a theorem for the pair function $g(r)$ due to Widom (1963) and the Ornstein–Zernike relation between $g(r)$ and $c(r)$, we can, at least for sufficiently small r, write $c(r)$ as a polynomial in r^2: $c(r) = \sum_{i=0}^{p} a_i r^{2i}$. By joining the small and large r behaviour at some intermediate point $r = r_0$, we can, for each p, determine all the parameters a_i except the scaling parameter r_0 by requiring that $c(r)$ together with its p first derivatives be continuous at $r = r_0$. This results in the following functional form for $c(r)$:

$$c(r) = -\beta V(r_0)\, f_p(r/r_0)$$

$$f_p(x) = \begin{cases} 1/x & x \geqslant 1 \\ [(2p+1)!!/p!2^p]\ {}_2F_1(\tfrac{1}{2}, -p; \tfrac{3}{2}; x^2) & x \leqslant 1 \end{cases} \tag{1}$$

where $x = r/r_0$ is the scaled distance while p denotes the number of continuous derivatives and ${}_2F_1(\frac{1}{2}, -p; \frac{3}{2}; x^2)$ is the hypergeometric function as defined by Gradshteyn and Ryzhik (1965), which in the present case is a polynomial of order p in x^2. Physically the direct correlation function $c(r)$ given by equation (1) can be thought of as due to the electrostatic potential of an effective ionic charge distribution inside a sphere of radius r_0. This effective ion-sphere radius r_0 will be determined below. Using a dimensionless Fourier transform, $f(\boldsymbol{k}) = n\int \mathrm{d}\boldsymbol{r}\, f(\boldsymbol{r}) \exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r})$, we obtain from equation (1), with the aid of Gradshteyn and Ryzhik (1965), the compact result

$$c(k) = -(k_D^2/k^2)\, h_p(kr_0) \tag{2}$$

where $k_D = (4\pi e^2 n\beta)^{1/2}$ is the Debye wavenumber and $h_p(y) = d_p(y)(2p+1)!!/y^p$, $d_p(y)$ being the spherical Bessel function of order p as defined in Gradshteyn and Ryzhik (1965). Hence for a given value of p, equation (2) shows that in this model $c(k)$ is a universal function of the scaled variable kr_0 with $b^2 = (k_D r_0)^2$ as amplitude. From equation (2) we can further obtain the static structure factor $S(k) = (1 - c(k))^{-1}$ and the dimensionless excess internal energy $U = (\beta e^2/\pi)\int_0^\infty \mathrm{d}k(S(k) - 1)$ from which the thermodynamic properties can be derived. For the isothermal compressibility χ_T we can obtain the virial compressibility via U or use the alternative definition

$$\chi_T^0/\chi_T = 1 - c^*(k = 0) \tag{3}$$

with $c(k) = -(k_D^2/k^2) + c^*(k)$ and $\chi_T^0 = \beta/n$, which was shown elsewhere (Baus 1978) to be equivalent to the virial compressibility. From equations (2)–(3) we find that in the present model the compressibility is given simply by

$$\chi_T^0/\chi_T = 1 - [k_D^2 r_0^2/2(3+2p)] \tag{4}$$

for the pth-order model. Before proceeding we pause a while to estimate theoretically the two characteristic Γ values of the OCP, i.e. the point $\Gamma = \Gamma_0$ at which the inverse compressibility changes sign ($\chi_T^{-1}(\Gamma_0) = 0$) and the point $\Gamma = \Gamma_1$ at which the OCP freezes. To this end we consider the first two simplest models, $p = 0$ and $p = 1$, and estimate roughly the effective radius r_0 by the mean ion-sphere radius ($r_0 \simeq a$). Taking into account that $k_D a = (3\Gamma)^{1/2}$, we obtain from equation (4) $\Gamma_0 = 2$ for $p = 0$ and $\Gamma_0 = 3{\cdot}3$ for $p = 1$, while the MC data yield $\Gamma_0 = 3{\cdot}08$. To estimate Γ_1 we use $r_0 \simeq a$ in equation (2) and look for the value of Γ for which the first peak of $S(k)$ diverges. This yields $\Gamma_1 = 53$ for $p = 0$ and $\Gamma_1 = 122$ for $p = 1$, while the MC results predict the fluid–solid phase transition to take place at $\Gamma = 155$.

As a second step we now determine the effective radius r_0 as a function of Γ and hence via equation (2) the Γ-dependence of $S(k)$ and of the thermodynamics. In order to do this in a simple manner, i.e. by a single numerical quadrature, we introduce a novel

HNC compressibility equation not previously found in the literature. We start from the exact relation, $g(r) \equiv 1 + h(r) = \exp(-\phi(r) + h(r) - c(r) + B(r))$ between the dimensionless pair potential $\phi(r) = \beta v(r)$, the pair correlation function $h(r)$, the direct correlation function $c(r)$ and the so-called Bridge contributions $B(r)$ (see for instance Ng 1974). Taking spatial gradients of both sides of this relation and rearranging terms we obtain, after multiplying the Fourier transform of each member by the scalar $\boldsymbol{k}/|\boldsymbol{k}|^2$:

$$c(k) = -\phi(k) + B(k) + \frac{1}{n}\int \frac{d\boldsymbol{k}'}{8\pi^3}\frac{\boldsymbol{k}.\boldsymbol{k}'}{k^2} h(|\boldsymbol{k} - \boldsymbol{k}'|)[h(k') - c(k') + B(k') - \phi(k')] \tag{5}$$

where, as above, all Fourier transforms are dimensionless. Using the Ornstein–Zernike relation $h(k) = c(k)/(1 - c(k))$ we can eliminate from equation (5) h in favour of c and obtain in the HNC approximation ($B = 0$)

$$c(k) = -\phi(k) + \frac{1}{n}\int \frac{d\boldsymbol{k}'}{8\pi^3}\frac{\boldsymbol{k}.\boldsymbol{k}'}{k^2} \frac{c(|\boldsymbol{k} - \boldsymbol{k}'|)[c(k')(c(k') + \phi(k')) = \phi(k')]}{[1 - c(|\boldsymbol{k} - \boldsymbol{k}'|)](1 - c(k'))} \tag{6}$$

which is a single closed non-linear integral equation for $c(k)$ in terms of $\phi(k)$ equivalent to the original r-space HNC system of equations. Equation (6) clearly shows that the HNC approximation for the OCP is consistent with the two familiar limiting results: $c(k) = -\phi(k)$, (i) for small k and all Γ and (ii) for all k and small Γ (Debye–Hückel approximation). Indeed for the OCP we have $\phi(k) = k_D^2/k^2$ and the first term in the RHS of equation (6) clearly dominates the second for $k \to 0$ and/or $\Gamma \to 0$. From equation (6) and equation (3) we immediately obtain

$$c^*(k = 0) = (1/6\pi^2 n)\int_0^\infty dk'\, k'^3[c^*(k') - h(k')]\, dh(k')/dk' \tag{7}$$

which is the desired HNC compressibility equation. The relation between r_0 and Γ which is needed to fix our model completely is obtained by requiring that equation (2) satisfies

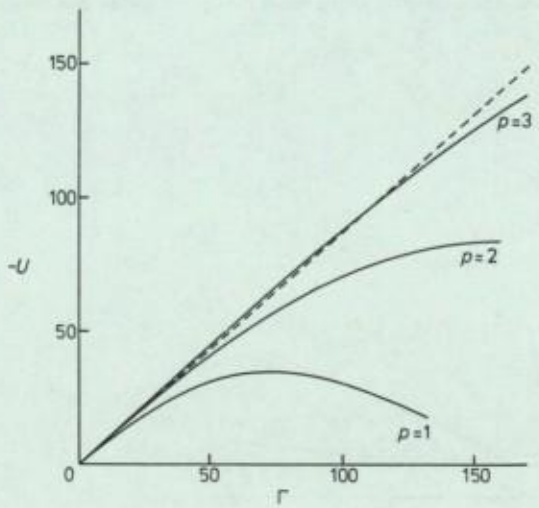

Figure 1. The dimensionless internal energy as a function of Γ from the present model (full curves) and from the interpolation formula of the HNC and MC data (broken line) proposed by De Witt (1976, 1978).

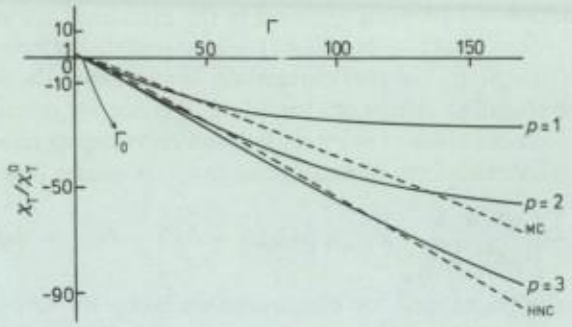

Figure 2. The inverse isothermal compressibility as a function of Γ. $\Gamma_0 = 3{\cdot}08$ for MC, $2{\cdot}76 < \Gamma_0 < 2{\cdot}97$ for $p = 3$, $2{\cdot}64 < \Gamma_0 < 2{\cdot}88$ for $p = 2$ and $2{\cdot}77 < \Gamma_0 < 2{\cdot}92$ for $p = 1$.

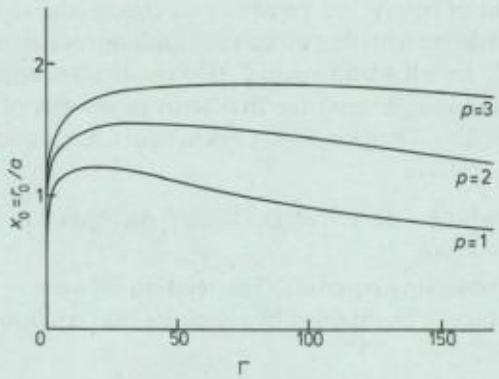

Figure 3. The ratio of the effective to the mean ion-sphere radius as a function of Γ.

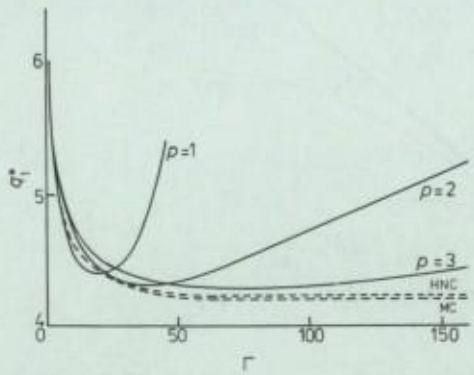

Figure 4. The position of the first peak of $S(k)$ in units of a^{-1} as a function of Γ. The MC data are taken from Galam and Hansen (1976) while the HNC data are from J P Hansen (unpublished).

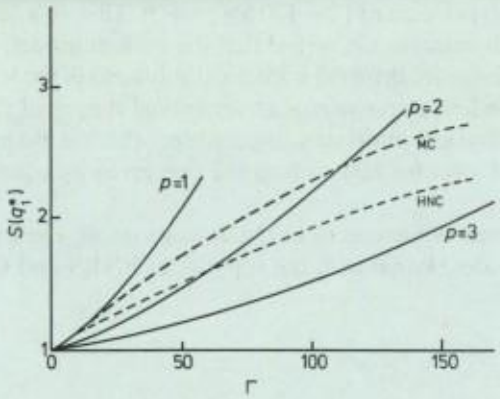

Figure 5. The amplitude of the first peak of $S(k)$ as a function of Γ. Data as in figure 4.

equation (7) exactly. This yields

$$\Gamma = \left(\frac{\pi\sqrt{3}}{4(3+2p)} \frac{k_D^2 r_0^2}{I_p(k_D r_0)} \right)^{2/3} \tag{8}$$

where $I_p(b)$ is given by the following quadrature:

$$I_p(b) = (1/b) \int_0^\infty \mathrm{d}x \{1 + [(2p+1)!!\, b^2 d_p(x)/x^{p+2}]^{-1}\}^{-1} \times \left[\frac{\frac{3}{2}(2p+1)!!\, d_p(x)/x^p}{1 + (2p+1)!!\, b^2 d_p(x)/x^{2+p}} + 1 - (2p+1)!! \frac{\mathrm{d}}{\mathrm{d}x} \left(\frac{d_p(x)}{x^{p-1}} \right) \right]. \tag{9}$$

We now have at our disposal an explicit functional form for $c(k)$, equation (2), depending on a single scale parameter r_0 which is given in terms of Γ by equation (8). As a final step we have computed equation (9) numerically for $p = 1, 2$ and 3 and for values of b (or Γ) covering the whole fluid phase. Our results are summarised in figures 1–5. As seen from the figures, the errors increase with increasing Γ for given p and decrease with increasing p for given Γ. From figure 1 we see that reasonable internal energies, compared with the HNC or MC data, are obtained up to $\Gamma = 25$ for $p = 1$, up to $\Gamma = 50$ for $p = 2$ while for $p = 3$ the error at $\Gamma = 160$ is still less than ten per cent. The fact that the $p = 3$ model yields the best results points to the existence of some amount of structure in the short-range part of $c(r)$. From figure 2 we see that the point at which the inverse compressibility vanishes ($\Gamma_0 = 2{\cdot}86$ for $p = 3$) is within the uncertainty of the MC data. For large Γ the compressibility tends however to its HNC value which differs markedly from the MC values. Clearly, on the basis of equation (7), we cannot expect to do better than the much more involved numerical solutions of the HNC equations themselves. From figure 3 we see that $b \equiv k_D r_0 = x_0(3\Gamma)^{1/2}$ rises monotonically with Γ whereas $x_0 = r_0/a$, i.e. the ratio of the effective to the mean ion-sphere radius, saturates for large Γ around $x_0 = 1{\cdot}8$ (for $p = 3$). This then in turn leads to a saturation of $c(r = 0)/\Gamma$ at a value of $-1{\cdot}23$ ($p = 3$) very close to the HNC ($-1{\cdot}22$) and MC ($-1{\cdot}33$) results. At the other extreme of small Γ, r_0 is seen from figure (3) to vanish with Γ, a result which guarantees that for weak coupling we recover the Debye–Hückel result which corresponds simply to $r_0 = 0$ in equation (2). From figures 4 and 5 we see that the position of the first peak (and in fact also of the other peaks) of $S(k)$ are quite well reproduced but that the amplitude of the

peak is much too low (about 30 per cent at $\Gamma = 170$ for $p = 3$). This, to a lesser extent, is also the case for the HNC data. In conclusion, we feel that the present model, while quantitatively not so outstanding as the more involved numerical solutions of the HNC equations, has the advantage of being the first step towards an analytical theory of the OCP statics for which it leads to a more physical understanding and for which it points to the existence of a universal functional form for $S(k)$ such as the one given by equation (2).

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