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Density Functional Approximations for Classical Fluids with Long-Range Interactions

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Density functional approximations for systems interacting via long-range forces are revisited. The theory is illustrated with examples of one-component plasmas in two and three dimensions.

KEY WORDS: Coulomb fluid; density functional; weighted density.

1. INTRODUCTION

The theory of inhomogeneous classical fluids in thermal equilibrium has progressed in two major directions. Most highly developed are integral equation methods, which can be sequentially corrected and lead to results of very high accuracy, but often at a computational cost that rivals that of computer simulations. Here, we will devote our attention to density functional methods, which are in a more rudimentary state. They give decent accuracy at low computational cost, but too often resemble recipes more than reliable logical procedures, and it is usually not clear how they are to be improved. Systematic improvement by means of integral equations techniques based upon entropy functional expansions is certainly possible,(1) but simplicity is sacrified in the process. A traditional approach under these circumstances is to push current practice to the point that its drawbacks become obvious and, more constructively, suggest improvements. The tool we use for pushing in this study is the Coulomb fluid, whose very long-range interaction renders it highly sensitive to approximations. In the particular

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Dedicated to Philippe Choquard, Coulomb fluid expert.

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case of a two-dimensional fluid at a special temperature, exact results are available, making comparison much easier to perform (see also Alastuey and Levesque(2, 3)). We will see that typical density functional formulations are inapplicable here, and focus on two that do apply, first in the context of the same two-dimensional model, and then for corresponding three-dimensional systems, in a slightly different context.

2. THE DENSITY FUNCTIONAL FORMAT

The undoubted progenitor of current density functional theory is the mean-field model of van der Waals. In terms of the "intrinsic" free energy

$$\bar{F}[n] = F - \int n(\mathbf{r})\, u(\mathbf{r})\, d\mathbf{r} \tag{1}$$

it takes the form

$$\begin{aligned} \bar{F} = {} & F^{\mathrm{id}}[n] + \int n(\mathbf{r})\, \Psi_o(n(\mathbf{r}))\, d\mathbf{r} \\ & + \tfrac{1}{2} \iint n(\mathbf{r})\, n(\mathbf{r}')\, \Delta\phi(\mathbf{r}-\mathbf{r}')\, d\mathbf{r}\, d\mathbf{r}' \end{aligned} \tag{2}$$

Here F is the Helmholtz free energy, $n(\mathbf{r})$ the particle density, and $u(\mathbf{r})$ the external potential. Entering into (2) is the implicit decomposition of the pair interaction potential, assumed to be the only internal interaction,

$$\phi(\mathbf{r}-\mathbf{r}') = \phi_o(\mathbf{r}-\mathbf{r}') + \Delta\phi(\mathbf{r}-\mathbf{r}') \tag{3}$$

into a short-range core ϕ_o and a long-range tail $\Delta\phi$, with

$$F^{\mathrm{id}} = \frac{1}{\beta} \int n(\mathbf{r})[\ln n(\mathbf{r}) - 1]\, d\mathbf{r} \tag{4}$$

the ideal gas free energy, and $\Psi_o(n)$ the excess free energy per particle of a uniform fluid of density n, reciprocal temperature β, in which only the core interaction is present. Qualitatively, (2) pictures the core fluid as locally uniform at any applicable scale of resolution. Equation (2) gives as well the profile equation

$$\begin{aligned} \mu(\mathbf{r}) &= \frac{\delta \bar{F}}{\delta n(\mathbf{r})} \\ &= \frac{1}{\beta} \ln n(\mathbf{r}) + \mu_o(n(\mathbf{r})) + \int n(\mathbf{r}')\, \Delta\phi(\mathbf{r}-\mathbf{r}')\, d\mathbf{r}' \end{aligned} \tag{5}$$

for the local chemical potential $\mu(\mathbf{r}) = \mu - u(\mathbf{r})$, $u(\mathbf{r})$ denoting the external potential that leads to the possible inhomogeneity [for $u(\mathbf{r}) \neq 0$], and $\mu_o(n)$ derived from $\Psi_o(n)$.

The information required by (2) is both meager—the equation of state $P_o(n)$—and experimentally nontrivial—the excess pair interaction $\Delta\phi(\mathbf{r}-\mathbf{r}')$. And the realm of quantitative validity is not extensive. To mitigate all three, one may modify (2) by the introduction of effective functions, to be determined by subsidiary numerical or physical experiment. Perhaps the simplest such modification, arising from a linear response expansion. is the generalization of the mean field $\int \Delta\phi(\mathbf{r}-\mathbf{r}')\, n(r)\, d\mathbf{r}$ seen by a particle at $\mathbf{r}'$ to the nonlinear version $\int W(\mathbf{r}-\mathbf{r}', n(\mathbf{r}))\, d(\mathbf{r})$, so that

$$\bar{F}[n] = \int n(\mathbf{r})\, f_o(n(\mathbf{r}))\, d\mathbf{r} + \tfrac{1}{2} \iint n(\mathbf{r}')\, W(\mathbf{r}-\mathbf{r}', n(\mathbf{r}))\, d\mathbf{r}\, d\mathbf{r}' \tag{6}$$

where f_o denotes the full free energy per particle in a uniform system, here with cores alone. Setting off the density pattern by a bar, it follows that

$$\mu(\mathbf{r} \mid n) = \mu_o(n(\mathbf{r})) + \tfrac{1}{2} \int W(\mathbf{r}-\mathbf{r}', n(\mathbf{r}'))\, d\mathbf{r}'$$

$$+ \tfrac{1}{2} \int n(\mathbf{r}')\, W'(\mathbf{r}-\mathbf{r}', n(\mathbf{r}))\, d\mathbf{r}' \tag{7}$$

where $W'(\mathbf{r}, n) = \partial W(\mathbf{r}, n)/\partial n$. Differentiating again yields the standard complete direct correlation function

$$C((\mathbf{r}, \mathbf{r}' \mid n) = \delta(\mathbf{r}-\mathbf{r}')/n(\mathbf{r}) - c_2(\mathbf{r}, \mathbf{r}' \mid n)$$

in the form

$$\frac{1}{\beta} C(\mathbf{r}, \mathbf{r}' \mid n) = \mu_o'(n(\mathbf{r}))\, \delta(\mathbf{r}-\mathbf{r}') + \frac{1}{2} W'(\mathbf{r}-\mathbf{r}', n(\mathbf{r}')) + \frac{1}{2} W'(\mathbf{r}-\mathbf{r}', n(\mathbf{r}))$$

$$+ \frac{1}{2} \int n(\mathbf{r}'')\, W''(\mathbf{r}-\mathbf{r}'', n(\mathbf{r}))\, d\mathbf{r}''\, \delta(\mathbf{r}-\mathbf{r}') \tag{8}$$

Only $W(\mathbf{r}-\mathbf{r}', n)$, a function of a vector variable and a scalar, has to be determined. This is done by assuming that the full uniform system direct correlation $C(\mathbf{r}-\mathbf{r}', n)$ is known, and with it, the thermodynamics via

$$\frac{1}{\beta} \int C(\mathbf{r}, n)\, d\mathbf{r} = \mu'(n) \tag{9}$$

$$\mu(\mathbf{r}) = \frac{d(nf(n))}{dn} \tag{10}$$

After a little algebra, (6) then reduces to

$$\bar{F}[n] = \int n(\mathbf{r})\, f(n(\mathbf{r}))\, d\mathbf{r} \\ - \frac{1}{4\beta} \iint (n(\mathbf{r}) - n(\mathbf{r}')) \int_{n(\mathbf{r}')}^{n(\mathbf{r})} C(\mathbf{r}-\mathbf{r}', n)\, dn\, d\mathbf{r}\, d\mathbf{r}' \tag{11}$$

The reference system is no longer needed, and the formulation is unchanged in the quantum domain, where, however, the bulk inverse linear response $C(\mathbf{r}-\mathbf{r}', n)$ is no longer related to the directly measurable static structure factor and no longer has a $\delta(\mathbf{r}-\mathbf{r}')/n$ singularity.

From (11) we have at once the profile equation

$$\mu(\mathbf{r} \mid n) = \mu(n(\mathbf{r})) - \frac{1}{2\beta} \iint_{n(\mathbf{r}')}^{n(\mathbf{r})} (C(\mathbf{r}-\mathbf{r}', n) + C(\mathbf{r}-\mathbf{r}', n(\mathbf{r})))\, dn\, d\mathbf{r}' \tag{12}$$

and the direct correlation

$$C(\mathbf{r}, \mathbf{r}' \mid n) = \tfrac{1}{2}(C(\mathbf{r}-\mathbf{r}', n(\mathbf{r})) + C(\mathbf{r}-\mathbf{r}', n(\mathbf{r}'))) \\ + \left[\mu'(n(\mathbf{r})) - \tfrac{1}{2} \int (n(\mathbf{r}) - n(\mathbf{r}''))\, C'(\mathbf{r}-\mathbf{r}'', n(\mathbf{r}))\, d\mathbf{r}'' \right] \delta(\mathbf{r}-\mathbf{r}') \tag{13}$$

The expression (11), which corrects in part the long-range mean-field aspect, is still deficient on small spatial scales, as signaled by the fact that (13) does not have the required $(1/n(\mathbf{r}))\, \delta(\mathbf{r}-\mathbf{r}')$ singularity. Indeed, the modifications that have preempted the field all in some fashion make use of an auxiliary weighted or effective density, representing a density in terms of which nominally local expressions attain short-scale validity as well. Simplest among these is that of Curtin and Ashcroft(4)

$$\bar{F}[n] = F^{\mathrm{id}} + \int n(\mathbf{r})\, \Psi(\nu(\mathbf{r}))\, d\mathbf{r} \tag{14}$$

in which the weighted density $\nu(\mathbf{r})$ has a density-dependent weight,

$$\nu(\mathbf{r}) = \int \omega(\mathbf{r}-\mathbf{r}', \nu(\mathbf{r}))\, n(\mathbf{r}')\, d\mathbf{r}' \tag{15}$$

$$\int \omega(\mathbf{r}, n)\, d\mathbf{r} = 1 \tag{16}$$

From (15)

$$\frac{\delta v(\mathbf{r})}{\delta n(\mathbf{r})}=\frac{\omega(\mathbf{r}-\mathbf{r}';v(\mathbf{r}))}{1-\int\omega'(\mathbf{r}-\mathbf{r}'';v(\mathbf{r}))\,n(\mathbf{r}'')\,d\mathbf{r}''} \tag{17}$$

so that (14) give rise to

$$\mu(\mathbf{r}\,|\,n)=\frac{1}{\beta}\ln n(\mathbf{r})+\Psi(v(\mathbf{r}))+\iint\frac{n(\mathbf{r}')\,\Psi'(v(\mathbf{r}'))\,\omega(\mathbf{r}-\mathbf{r}',v(\mathbf{r}'))}{1-\int\omega'(\mathbf{r}'-\mathbf{r}'',v(\mathbf{r}'))\,n(\mathbf{r}'')\,d\mathbf{r}''}\,d\mathbf{r}' \tag{18}$$

and then to

$$\begin{aligned}\frac{1}{\beta}C(\mathbf{r},\mathbf{r}'\,|\,n)=&\frac{\delta(\mathbf{r}-\mathbf{r}')}{\beta n(\mathbf{r})}+\frac{\Psi'(v(\mathbf{r}))\,\omega(\mathbf{r}-\mathbf{r}',v(\mathbf{r}))}{1-\int\omega'(\mathbf{r}-\mathbf{r}'',v(\mathbf{r}))\,n(\mathbf{r}'')\,d\mathbf{r}''}\\&+\frac{\Psi'(v(\mathbf{r}'))\,\omega(\mathbf{r}-\mathbf{r}',v(\mathbf{r}'))}{1-\int\omega'(\mathbf{r}'-\mathbf{r}'',v(\mathbf{r}'))\,n(\mathbf{r}'')\,d\mathbf{r}''}\\&+\int\frac{n(\mathbf{R})}{[1-\int\omega'(\mathbf{R}-\mathbf{r}'',v(\mathbf{R}))\,n(\mathbf{r}'')\,d\mathbf{r}'']^2}\\&\quad\frac{\partial}{\partial v(\mathbf{r})}\cdot\Psi'(v(\mathbf{R}))\,\omega(\mathbf{r}-\mathbf{R},v(\mathbf{R}))\,\omega(\mathbf{r}'-\mathbf{R},v(\mathbf{R}))\,d\mathbf{R}\\&+\iint\frac{n(\mathbf{R})\,n(\mathbf{R}')}{[1-\int\omega'(\mathbf{R}-\mathbf{r}'',v(\mathbf{R}))\,n(\mathbf{r}'')\,d\mathbf{r}'']^3}\\&\times\Psi'(v(\mathbf{R}))\,\omega(\mathbf{r}-\mathbf{R},v(\mathbf{R}))\,\omega''(\mathbf{R}-\mathbf{R}',v(\mathbf{R}))\\&\times\omega(\mathbf{R}-\mathbf{r}',v(\mathbf{R}))\,d\mathbf{R}\,d\mathbf{R}'\end{aligned} \tag{19}$$

To find ω, one again compares with $C(\mathbf{r}-\mathbf{r}',n)$ at uniform $n(\mathbf{r})=n$. From $\int\omega(\mathbf{r},n)\,d\mathbf{r}=1$, and Fourier transforming, (19) yields

$$\begin{aligned}0=&\,2n\Psi'(n)\,\tilde{\omega}(k,n)\,\tilde{\omega}'(k,n)+n\Psi''(n)\,\tilde{\omega}^2(k,n)\\&+2\Psi'(n)\,\tilde{\omega}(k,n)+\frac{1}{\beta}\tilde{c}_2(k,n)\end{aligned} \tag{20}$$

In general, (20) must be solved numerically, but without doing so, two things are clear: (1) Eq. (19) has exactly the correct short-range singularity, but (2) if $\tilde{c}_2$ is lông range, i.e., diverges as $k\to 0$, then so is $\tilde{\omega}$, leading to a very smeared-out weighted density. In fact, for Coulombic interaction, one sees that $\tilde{\omega}(k,n)\propto 1/k$ at low k and no normalizable weight function exists.

An obvious next step, following Meister and Kroll(5) and Groot and van der Eerden,(6) is to introduce an effective density into both local free energy and mean-field potential, in the form

$$\bar{F}[n, v] = F^{\text{id}}[n] + \int n(\mathbf{r})\, \Psi_o(v(\mathbf{r}))\, d\mathbf{r} \\ + \tfrac{1}{2} \iint n(\mathbf{r}')\, n(\mathbf{r})\, \omega(\mathbf{r} - \mathbf{r}'),\, v(\mathbf{r}))\, d\mathbf{r}\, d\mathbf{r}' \tag{21}$$

Since ω already supplies a parametric function of a vector and scalar, it is not necessary to require the same for the weight function associated with $v(\mathbf{r})$; it suffices to make (21) variational with respect to n and v (not necessarily a minimum):

$$\mu(\mathbf{r} \,|\, n) = \frac{\delta \bar{F}[n, v]}{\delta n(\mathbf{r})} \tag{22}$$

$$0 = \frac{\delta \bar{F}[n, v]}{\delta v(\mathbf{r})} \tag{23}$$

Thus,

$$\mu(\mathbf{r} \,|\, n) = \frac{1}{\beta} \ln n(\mathbf{r}) + \Psi_o(v(\mathbf{r})) + \frac{1}{2} \int n(\mathbf{r}')\, \omega(\mathbf{r} - \mathbf{r}', v(\mathbf{r}))\, d\mathbf{r}' \\ + \frac{1}{2} \int n(\mathbf{r}')\, \omega(\mathbf{r} - \mathbf{r}', v(\mathbf{r}'))\, d\mathbf{r}' \tag{24}$$

where

$$0 = \Psi_o'(v(\mathbf{r})) + \tfrac{1}{2} \int n(\mathbf{r})\, \omega'(\mathbf{r} - \mathbf{r}', v(\mathbf{r}))\, d\mathbf{r}' \tag{25}$$

It follows from (24) that

$$\frac{\delta v(\mathbf{r})}{\delta n(\mathbf{r}')} = \frac{-\tfrac{1}{2}\omega'(\mathbf{r} - \mathbf{r}', v(\mathbf{r}))}{\Psi_o''(v(\mathbf{r})) + \tfrac{1}{2} \int n(\mathbf{r}'')\, \omega''(\mathbf{r} - \mathbf{r}'', v(\mathbf{r}))\, d\mathbf{r}''} \tag{26}$$

and so, from (24), using (25) as well,

$$\frac{1}{\beta} C(\mathbf{r}, \mathbf{r}' \,|\, n) = \frac{\delta(\mathbf{r} - \mathbf{r}')}{\beta n(\mathbf{r})} + \frac{1}{2} \omega(\mathbf{r} - \mathbf{r}', v(\mathbf{r})) + \frac{1}{2} \omega(\mathbf{r} - \mathbf{r}', v(\mathbf{r}')) \\ - \frac{1}{4} \int \frac{\omega'(\mathbf{r} - \mathbf{R}, v(\mathbf{R}))\, \omega'(\mathbf{R} - \mathbf{r}', v(\mathbf{R}))\, n(\mathbf{R})}{\Psi_o''(v(\mathbf{R})) + \tfrac{1}{2} \int n(\mathbf{R}')\, \omega''(\mathbf{R} - \mathbf{R}', v(\mathbf{R}))\, d\mathbf{R}'}\, d\mathbf{R} \tag{27}$$

Specializing to the uniform system, we then require

$$-\frac{1}{\beta}\tilde{c}_2=\tilde{\omega}(k,n)+\frac{1}{2}\frac{n(\tilde{\omega}'(k,n))^2}{\tilde{\omega}'(0,n)} \tag{28}$$

Note that $\tilde{\omega}(0,n)$, and hence $\Psi_o(n)$, are now determined by the bulk thermodynamics. Once more, as with (20), the Coulomb interaction picks up a very long-range contribution to $\omega(r,n)$. Here, however, normalization of ω is not required; a long-range *density-independent* component of ω will affect only the interaction parts of (21) and (24), and this turns out to be innocuous. The hint supplied in this fashion will play a crucial role in the reformulation of (14)–(16) that we will suggest.

3. THE TWO-DIMENSIONAL, ONE-COMPONENT PLASMA

In order to assess the adequacy of approximation methods, one needs a nontrivial system that has been solved exactly. The well-known and virtually unique example of such a system, incorporating long-range forces as well, is the two-dimensional Coulomb gas with point particles of charge q in a rigid homogeneous background. In the usual normalization, the pair potential is given by

$$\phi(r)=-q^2\ln(r/L) \tag{29}$$

where L is a suitable length required if only for dimensional reasons. At a temperature such that $\Gamma=\beta q^2=2$, this model is exactly solvable even in a number of nonuniform cases. For the uniform system at density n, it is known(7) that the pair-correlation function $h(r)=g(r)-1$ is given by

$$h(r)=-e^{-\pi n r^2} \tag{30}$$

and from the convolution identity

$$n\left(\frac{1}{m}e^{-\pi n r^2/m}-\frac{1}{m}\right)*e^{-\pi n r^2}=\frac{1}{m+1}e^{-\pi n r^2/(m+1)}-\frac{1}{m} \tag{31}$$

it follows that

$$c_2^o(r)=-\sum_{m=1}^{\infty}\frac{1}{m}(e^{-\pi n r^2/m}-1) \tag{32}$$

satisfies the Ornstein–Zernike equation $h-c_2=nh*c_2$ for the direct correlation function. However, $c_2(r)$ is undetermined to an additional constant, because $nh*1=-1$ in the present case. For long-range forces, one expects that $c_2(r)\to-\beta\phi(r)$ as $r\to\infty$, and it will be particularly convenient to arrange the additive normalization of c_2 so that $c_2(r) + \ln(r^2/L^2) \to 0$ as $r \to 0$. For this purpose, we use the identity

$$1 - e^{-\pi n r^2/m} = \int_0^\infty J_1(k)\, e^{-mk^2/4\pi n r^2}\, dk \tag{33}$$

where J_1 is a Bessel function, so that

$$c_2^o = \int_0^\infty J_1(k) \ln(1 - e^{-k^2/4\pi n r^2})\, dk \tag{34}$$

Hence

$$\lim_{r \to \infty} c_2^o(r) + \ln(r^2/L^2) = \int_0^\infty J_1(k) \ln(k^2/4\pi n L^2)\, dk \tag{35}$$

$$= -2\gamma - \ln(\pi n L^2) \tag{36}$$

where $\gamma = -\Gamma'(1)$ is Euler's constant. We conclude that

$$c_2(r) = c_2^o(r) + 2\gamma + \ln(\pi n L^2) \tag{37}$$

is the correctly normalized function.

For an inhomogeneous system to serve as test case for assessing approximations, we choose an idealization which is not far from a situation of interest, that of an infinite fluid of asymptotic density n bounded by a hard wall for $x \leqslant 0$. Jancovici[8] has calculated the resulting particle density

$$n(x) = \frac{2n}{\sqrt{\pi}} \int_0^\infty \frac{\exp[-(t - x(2n\pi)^{1/2})^2]}{1 + \Phi(t)}\, dt \tag{38}$$

where x is the distance to the wall, and $\Phi(t)$ the error function

$$\Phi(t) = \frac{2}{\sqrt{\pi}} \int_0^t \exp(-u^2)\, du \tag{39}$$

In greater detail he found that the total correlation function is given by

$$h(x_1, y_1, x_2, y_2)$$

$$= -\exp[-n\pi(x_1 - x_2)^2]\, \frac{4}{\pi} \tag{40}$$

$$\times \left| \int_0^\infty \frac{\exp\{-[t - (x_1 + x_2)(n\pi/2)^{1/2}]^2 - it(y_1 - y_2)(2n\pi)^{1/2}\}}{1 + \Phi(t)}\, dt \right|^2 \tag{41}$$

where x_1, x_2 are the coordinates perpendicular to the wall, and y_1 and y_2 those parallel to the wall.

4. MODIFIED DENSITY FUNCTIONALS

The very long-range, even divergent, form of $c_2(r)$ for the one-component plasma renders unsuitable the usual weighted density functionals, since the weight function ω always picks up some of the long-range character. The simplest cure is to eliminate the long-range interaction at least in mean-field form, at the outset. For example, an intermediate between (14) and (21) is

$$\bar{F} = F^{\mathrm{id}}[n] + \int n(\mathbf{r})\, \Psi(v(\mathbf{r}))\, d\mathbf{r} + \tfrac{1}{2} \iint (n(\mathbf{r}) - n)(n(\mathbf{r}') - n)\, \Delta\phi(\mathbf{r} - \mathbf{r}')\, d\mathbf{r}\, d\mathbf{r}' \tag{42}$$

Note that we have included a neutralizing background (for Coulomb forces) of density n, corresponding to a Hamiltonian whose interaction is taken as

$$\tfrac{1}{2}\Delta\phi(\mathbf{r}_i - \mathbf{r}_j) - \int n\, \Delta\phi(\mathbf{r}_i - \mathbf{r})\, d\mathbf{r} + \tfrac{1}{2} \iint n^2\, \Delta\phi(\mathbf{r} - \mathbf{r}')\, d\mathbf{r}\, d\mathbf{r}'$$

is any finite domain.

Equation (42) is in fact identical with an expression suggested some years ago by Tarazona and Evans,(9) but rather than follow their approach and guess reasonable forms for the effective density v, we again construct it as in (15) from the weight ω, and determine ω by reproducing the uniform fluid correlation structure; see also Jones and Gunnarsson.(10) Proceeding precisely as in (15), we now have

$$\mu(\mathbf{r} \mid n) = \frac{1}{\beta} \ln n(\mathbf{r}) + \Psi(v(\mathbf{r})) + \int (n(\mathbf{r}) - n)\, \Delta\phi(\mathbf{r} - \mathbf{r}')\, d\mathbf{r}' + \int \frac{n(\mathbf{r}')\, \Psi'(v(\mathbf{r}'))\, \omega(\mathbf{r} - \mathbf{r}', v(\mathbf{r}'))}{1 - \int \omega'(\mathbf{r}' - \mathbf{r}'', v(\mathbf{r}'))\, n(\mathbf{r}'')\, d\mathbf{r}''}\, d\mathbf{r}' \tag{43}$$

from which $C(\mathbf{r}, \mathbf{r}' \mid n)$ is computed, and (20) replaced by

$$0 = 2n\Psi'(n)\, \tilde{\omega}(k, n)\, \tilde{\omega}'(k, n) + n\Psi''(n)\, \tilde{\omega}^2(k, n) + 2\Psi'(n)\, \tilde{\omega}(k, n) + \frac{1}{\beta}\tilde{c}_2(k, n) + \Delta\tilde{\phi}(k) \tag{44}$$

Indeed, as a result of this modification, only the combination $c_2 + \beta\, \Delta\phi$ occurs, so that long-range terms do not appear.

There is another option, which is to work directly with the "profile equation" for $\mu(\mathbf{r}\,|\,n)$. For example, a locally homogeneous effective density profile equation corresponding to (14) would be

$$\mu(\mathbf{r}\,|\,n)=\frac{1}{\beta}\ln n(\mathbf{r})+\mu_{\mathrm{ex}}(\nu(\mathbf{r})) \tag{45}$$

and so the corresponding mean-field subtracted version would take the form

$$\mu(\mathbf{r}\,|\,n)=\frac{1}{\beta}\ln n(\mathbf{r})+\mu_{\mathrm{ex}}(\nu(\mathbf{r}))+\int (n(\mathbf{r}')-n)\,\Delta\phi(\mathbf{r}-\mathbf{r}')\,d\mathbf{r}' \tag{46}$$

Differentiating, using (4), and evaluating at uniformity, we replace (44) by the much simpler

$$\mu'_{\mathrm{ex}}(n)\,\omega(\mathbf{r},n)+\frac{1}{\beta}(c_2(\mathbf{r},n)+\beta\,\Delta\phi(\mathbf{r}))=0. \tag{47}$$

Again, as in (44), the long-range pathology does not affect $\omega(\mathbf{r})$. Of course, both (43) and (46) suffer from the simultaneous advantage and disadvantage that the precise subtraction of $\Delta\phi(\mathbf{r})$ is up to the practitioner. And (46) has the same in-principle drawback as does (45), that it is not integrable, i.e., does not come from the variation of a free energy. One knows that this can produce inconsistencies if used carelessly, but that they can be avoided. To be sure, an expression of the simplicity of (47) has been obtained by Denton and Ashcroft in the free energy format(11) tailored for periodic inhomogeneities, in which the idea of a uniform effective density makes sense, and also in the one-particle direct correlation function format.(12) These authors also used (45) to generate approximations to higher distribution functions.

5. SUM RULES

In assessing an approximation method, it is clearly useful to have, in addition to the full profile, single quantities that can serve as figures of merit. There are many such sum rules, almost all derivable from the classical statistical mechanical identity

$$\langle A\,\Delta\beta\Phi\rangle=\langle\nabla A\rangle \tag{48}$$

for any observable A, any coordinate derivative ∇, and the full potential energy Φ. In general, this involves multisite correlations, and thereby requires detailed information, whose accuracy one cannot reasonably demand. In the case of a Coulomb interaction fluid, constrained by a plane boundary, there are nontrivial sum rules depending only on a one-dimensional one-site density profile. Physically they result from the perfect shielding of the classical plasma and the fact that the boundary used, an ideal insulating plane, can have no charge accumulation.

Actually the most useful form of (48) is that in which A is the microscopic density of a specified particle and ∇ the corresponding gradient. This gives rise to the second of the YBG hierarchy

$$\nabla n(\mathbf{r}) = n(\mathbf{r})\,\nabla\beta u(\mathbf{r}) + \int n_2(\mathbf{r},\mathbf{r}')\,\nabla\beta\phi(\mathbf{r}-\mathbf{r}')\,d\mathbf{r}' = 0 \tag{49}$$

In the present case, the only external potential is a rigid wall, but there is a uniform background of negative source interactions; thus (49) becomes

$$\nabla n(\mathbf{r}) = \int (n_2(\mathbf{r},\mathbf{r}') - n(\mathbf{r})n)\,\nabla\beta\phi(\mathbf{r}-\mathbf{r}')\,d\mathbf{r}' = 0 \tag{50}$$

inside the accessible volume. At the temperature corresponding to $\Gamma = 2$ in the two-dimensional Coulomb fluid, $\beta\phi(r) = -\ln(r^2/L^2)$, so that for the plane symmetric configuration of interest, (50) reduces to

$$\begin{aligned} n'(x) &= -2\int (n_2(x,x',y-y') - n(x)n)\,\frac{x-x'}{(x-x')^2+(y-y')^2}\,dx'\,dy' \\ &= -2\int (n_2(x,x',y-y') - n(x)\,n(x'))\,\frac{x-x'}{(x-x')^2+(y-y')^2}\,dx'\,dy' \\ &= -2\pi\int (n(x')-n)\,n(x)\,\mathrm{sgn}(x-x')\,dx' \end{aligned} \tag{51}$$

Taking the limit $x \to \infty$ in (51) yields

$$\int_0^\infty (n(x')-n)\,dx' = 0 \tag{52}$$

which is the perfect shielding sum rule.

Choquard *et al.*[13] derived relations between different definitions of the pressure for one-component systems with long-range forces, among them

$$\beta p^{(k)} - \beta p^{(\theta)} = 2\pi\Gamma\int_0^\infty x(n(x)-n)\,dx \tag{53}$$

where the kinetic pressure is

$$\beta p^{(k)} = n(0) \tag{54}$$

and the thermal pressure is

$$\beta p^{(\theta)} = n\left(1 - \frac{\Gamma}{4}\right) \tag{55}$$

which can be written as the sum rule

$$2\pi\Gamma \int_0^\infty x(n(x) - n)\, dx = n(0) - n\left(1 - \frac{\Gamma}{4}\right) \tag{56}$$

How well do our approximations fare with respect to (52) and (56)? Both approximations of Section 4 have the form

$$\Delta(\mathbf{r}) = \int n(\mathbf{r}') - n)\beta\, \Delta\phi(\mathbf{r} - \mathbf{r}')\, d\mathbf{r}' \tag{57}$$

We will choose $\beta\, \Delta\phi = \beta\phi$, the full potential, so that in the plane geometry

$$\begin{aligned} \Delta'(x) &= -2\pi \int_0^\infty (n(x') - n)\, \mathrm{sgn}(x - x')\, dx' \\ &= 2\pi \int_x^\infty (n(x') - n)\, dx' - 2\pi \int_0^x (n(x') - n)\, dx' \end{aligned} \tag{58}$$

and in particular

$$\Delta'(\infty) = -2\pi \int_0^\infty (n(x') - n)\, dx' \tag{59}$$

Now in absence of external fields inside the accessible volume, the approximations of Section 4 read, respectively,

$$\begin{aligned} \Delta(\mathbf{r}) = \ln n - \ln n(\mathbf{r}) + \beta\mu_{\mathrm{ex}}(n) - \Psi(\nu(\mathbf{r})) \\ - \int \frac{n(\mathbf{r}')\, \Psi'(\nu(\mathbf{r}'))\, \omega(\mathbf{r} - \mathbf{r}', \nu(\mathbf{r}'))}{1 - \int \omega'(\mathbf{r}' - \mathbf{r}'', \nu(\mathbf{r}'))\, n(\mathbf{r}'')\, d\mathbf{r}''}\, d\mathbf{r}' \end{aligned} \tag{60}$$

$$\Delta(\mathbf{r}) = \ln n - \ln n(\mathbf{r}) + \beta\mu_{\mathrm{ex}}(n) - \beta\mu_{\mathrm{ex}}(\nu(\mathbf{r})) \tag{61}$$

Since $n(\mathbf{r})$ and $\nu(\mathbf{r})$ approach n very rapidly as $x \to \infty$, and $\int \omega(\mathbf{r}, \nu)\, d\mathbf{r} = 1$, $\int \omega'(\mathbf{r}, \nu)\, d\mathbf{r} = 0$, $\beta\mu_{\mathrm{ex}}(n) = \Psi(n) + n\Psi'(n)$, it is easily shown that $\Delta'(\infty) = \Delta(\infty) = 0$ in both cases, so that (57) is satisfied.

From (58), now in the form $\Delta'(x)=4\pi\int_x^\infty (n(x')-n)\,dx'$, it follows that

$$-\Delta(0)=4\pi\int_0^\infty (n(x')-n)\,dx' \tag{62}$$

By virtue of the very simple $\beta F_{\mathrm{ex}}/N=-\frac{1}{2}\ln n+1-\frac{1}{2}\ln(2\pi^2L^2)$ for the uniform Coulomb fluid, we have

$$\beta\mu_{\mathrm{ex}}=C-\tfrac{1}{2}\ln n \tag{63}$$

$$\beta\Psi=C'-\tfrac{1}{2}\ln n \tag{64}$$

for suitable constants C, C' and the two weight functions thereby reduce to

$$\frac{1}{2}\tilde{\omega}(k,n)-\frac{1}{2n}\tilde{\omega}^2(k,n)+\tilde{\omega}(k,n)\,\tilde{\omega}'(k,n)=\tilde{c}_2(k,n)+\beta\tilde{\phi}(k) \tag{65}$$

$$\frac{1}{2n}\,\omega(r,n)=c_2(r,n)+\beta\phi(r) \tag{66}$$

in the two cases. However, there seems to be no direct connection between (60), (61), (65), and (66) and the sum rule (56). The comparison will have to be made numerically.

6. TWO-DIMENSIONAL WALL-BOUNDED PLASMA: NUMERICAL CALCULATION

Let us now compare the two approximation schemes with exact results for the two-dimensional, one-component plasma bounded by an ideal wall. As mentioned above, we choose the full interaction $\Delta\phi(\mathbf{r})=\phi(\mathbf{r})$ for the mean-field component. For both approximations, our numerical iterations start from the exact density profile and then minimize the difference between the bulk chemical potential and the right-hand side of (43) and (46) at each grid point. In principle, there is no need of choosing bulk density other than $n=1$, since the profile scales trivially with density: $n(x)/n=f(n^{1/2}x)$, but we have done so anyway as a test of our primitive minimization procedure.

The calculations for the two approximations are similar, and some parts even identical. An example is the integral term in the chemical potential:

$$\begin{aligned}\mu_c(\mathbf{r})&=\int [n(\mathbf{r})-n]\,\beta\phi(\mathbf{r}-\mathbf{r}')\,d\mathbf{r}'\\ &=-\int_{-\infty}^{\infty}\int_0^{\infty}[n(x')-n]\ln[(x-x')^2+y'^2]\,dx'\,dy'\end{aligned} \tag{67}$$

[the $\ln L$ term vanishes according to charge neutrality, (55)], which we rewrite as

$$-\int_{-\infty}^{\infty}\int_{0}^{\infty}\ln[(x-x')^2+y'^2]\,dx'\,dy'\int_{0}^{x'}[n(z)-n]\,dz \tag{68}$$

$$=\int_{-\infty}^{\infty}\int_{0}^{\infty}\int_{0}^{x'}[n(z)-n]\,dz\,\frac{2(x-x')}{(x-x')^2+y'^2}\,dy'\,dx' \tag{69}$$

and hence as

$$\mu_c(x)=2\pi\int_{0}^{\infty}\operatorname{sgn}(x-x')\left\{\int_{0}^{x'}[n(z)-n]\,dz\right\}dx' \tag{70}$$

Charge neutralization sets in very rapidly and carrying the integration to $x'=10$ introduces negligible errors.

The calculation of the weight function ω in the first approximation must be performed numerically. We solve its equation iteratively as

$$\tilde{\omega}_{j+1}=\frac{\tilde{c}_2+\beta\tilde{\phi}}{1/2-(1/2n)\tilde{\omega}_j+\tilde{\omega}_j'} \tag{71}$$

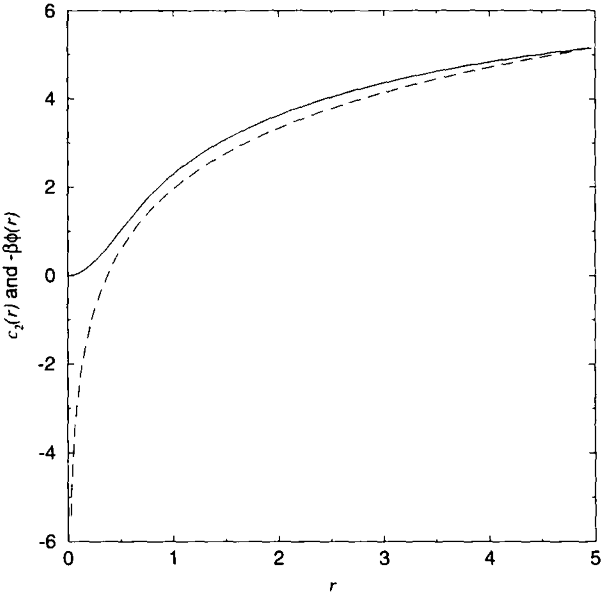

Fig. 1. The negative pair potential $-\beta\phi(r)$ (dashed line) and direct correlation function $c_2(r)$ (solid line) when they are set equal at $r=5$. In the calculation they are set equal at $r=10$.

and Hankel transform back to real space. The resulting weight function has more mass at larger r than does $c_2 + \beta\phi$ and truncation at $r = 10$ may give rise to values of the density that are too high.

A comparison of approximations and exact profile (Fig. 2) shows that (a) the approximations overestimate the density close to the wall and underestimate it further away from the wall; the simple minimization procedure is not perfect, but the difference in chemical potential from the bulk value decreases to around 5% of what it is for the exact profile, which served as a start for the calculation; and (b) the two approximations are nearly indistinguishable in this case. In Fig. 3 different densities are used to check the minimization procedures. The minimization is started from the same profile in all cases, and the increment is larger than for the comparison of approximations, which is the reason for the different contact values. In any event, the contact values in Fig. 2 are certainly improved over what was obtained in the investigation by Alastuey *et al.* of some other density functional approximations.[2, 3] Evaluation of sum rules (52) and (56) shows charge neutrality within the accuracy of the calculation,

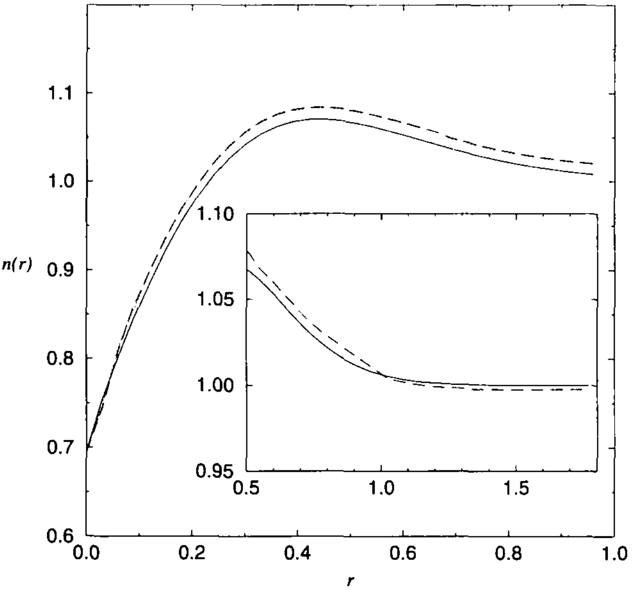

Fig. 2. Density profiles $n(r)$ for the two approximations [dotted and dashed lines for Eqs. (42) and (46), respectively] against the exact but numerically evaluated one (solid line) for bulk density $n = 1$. The inset shows that the approximate curves cross the exact one, and do not violate charge neutrality within the accuracy given by the primitive minimization procedure.

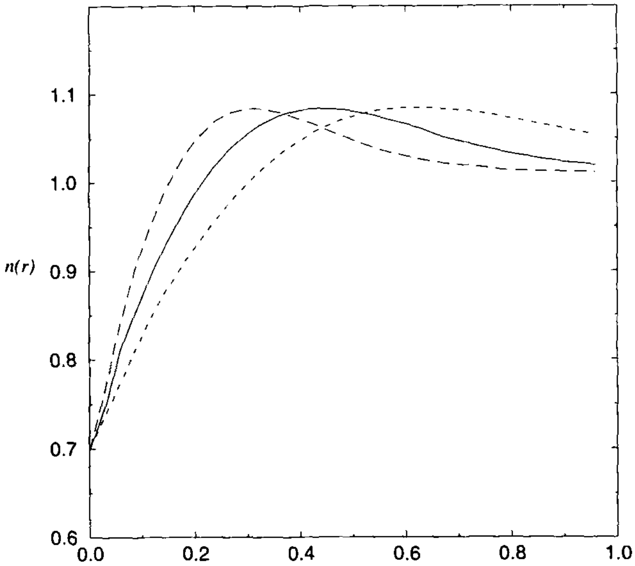

Fig. 3. Normalized profiles for the first approximation and three bulk densities $n = 0.5$, 1, 2 (dashed, solid, long-dashed). The profiles result from the same start profile, and can be regarded as a test of the minimization procedure.

and good agreement with (56) if the calculation is truncated at $r = 2$. The minimization procedure with its finite increment in density results in a small deviation from the "real" profile, which gives large contributions to the integral in (56) at large r.

7. THREE-DIMENSIONAL PLASMA

Since the two approximations produce in our test case results that are similar, this suggests that we stick to the simpler version (46), (47). A further check of its adequacy would be welcome. There are no further exactly solved long-range interaction models to rely on, so we turn instead to the more realistic three-dimensional, one-component plasma, not restricted to a single coupling constant. It is known from comparisons with simulations that the HNC integral equation is very accurate for a wide range of couplings. Since most extensive HNC results are available for the uniform plasma, and they of course include the two-site distribution function, let us take advantage of this by recasting the system as a nonuniform one. That is, we recall that the pair density of bulk fluid is obtainable from the density at one site with a particle fixed at another site, and the latter to its equivalent external potential:

$$n_2(\mathbf{r}, \mathbf{r}') = n(\mathbf{r} \mid \mathbf{r}')\, n(\mathbf{r}') = n(\mathbf{r} \mid u_{\phi, \mathbf{r}'}) \tag{72}$$

where

$$u_{\phi, \mathbf{r}'}(\mathbf{r}) = \phi(\mathbf{r} - \mathbf{r}') \tag{73}$$

so that

$$g(r) = n(r \mid u_{\phi, 0})/n \tag{74}$$

Thus we can compare predictions of our approximation under the special external potential $u_{\phi,0}$ with the accurate HNC solution for $g(r)$.

For a three-dimensional Coulomb system, the dimensionless coupling constant is taken as

$$\Gamma = \beta q^2 (\tfrac{4}{3}\pi n)^{1/3} \tag{75}$$

where n is the bulk density and hence the asymptotic density of our non-uniform fluid. At fixed Γ, the density profile now scales as $n(r)/n = f(n^{1/3} r)$, so that we are free to set units to give n any desired value, which we will here take as $n = 3/4\pi$.

In the system under study, the basic profile equation in our approximation becomes

$$\ln n + \beta\mu_{\text{ex}}(n) + \frac{\beta q^2}{r} = \ln n(r) + \beta\mu_{\text{ex}}(\nu(r)) + \int \frac{\beta q^2}{|\mathbf{r} - \mathbf{r}'|} (n(\mathbf{r}') - n)\, d\mathbf{r}' \tag{76}$$

now translated as

$$g(r) = \exp\left[\beta\mu_{\text{ex}}(n) - \beta\mu_{\text{ex}}(\nu(r)) + \frac{\beta q^2}{r} - \beta q^2 n \int \frac{h(r')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \right] \tag{77}$$

where $h = g - 1$, and the weight function is given by

$$\omega(r) = \frac{1}{\beta\mu'_{\text{ex}}(r)} \left(c_2(r, n) + \frac{\beta q^2}{r} \right) \tag{78}$$

Since exact information need not be consistent with a given approximation, we cannot assume that $\mu'_{\text{ex}}(n)$ and $c_2(r, n)$ are already known. Rather, $c_2(r, n)$ is determined by the Ornstein–Zernike definition

$$c_2(r, n) = h(r, n) - n \int h(\mathbf{r} - \mathbf{r}', n)\, c_2(r', n)\, d\mathbf{r}' \tag{79}$$

and μ_{ex} by

$$\beta\mu_{\text{ex}}(n) = -\int_0^n \int \left(c_2(r', n') + \frac{\beta q^2}{r'} \right) d\mathbf{r}'\, dn' \tag{80}$$

The defining relation

$$v(r) = \int \omega(\mathbf{r} - \mathbf{r}', v(r))\, n(r')\, d\mathbf{r}' \tag{81}$$

is of course unchanged.

In solving the approximation (77)–(81), there are several sources of numerical instability which can be recognized and guarded against. One is that, taking $r \to \infty$ in (76), the exact solution must satisfy

$$n \int h(r, n)\, d\mathbf{r} = -1 \tag{82}$$

the charge neutrality condition for the one-ion source. If (82) is not

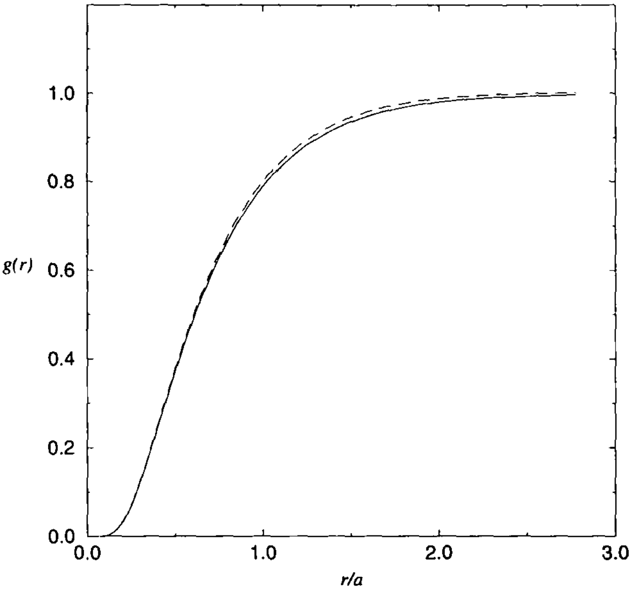

Fig. 4. The pair distribution function $g(r)$ for coupling constant $\Gamma = 0.9$ from the hypernetted chain approximation (dashed line) and from the density functional approximation (solid lines) after 20, 50, and 80 iterations. The latter three functions overlap. The radius is dimensionless, r/a, where $a = (3/4\pi n)^{1/3}$.

satisfied, then (77) will produce a nonvanishing h for large r, which further exacerbates the failure of (77). We have therefore enforced (82) by renormalizing the g obtained from (77).

Another problem concerns the long-range behavior of $c_2(r, n)$, which must cancel that of $\beta\phi(r)$ to give the correct behavior of $\omega(r)$ in (78). This means that $\tilde{c}_2(k, n)$ is singular at $k = 0$, a singularity that is equivalent to (82). But it is not singular at $r = 0$. One way of controlling this behavior is to add to c_2 not $\beta\phi$, but the "help-function"

$$\beta\phi_h(r) = \frac{\beta q^2}{r}(1 - e^{-\alpha r}) \tag{83}$$

for which

$$\beta\tilde{\phi}_h(k) = 4\pi\beta q^2 \frac{\alpha^2}{k^2(k^2 + \alpha^2)} \tag{84}$$

is also exactly known. If $\alpha \gg \Delta k$, the k-space grid spacing, $\tilde{\phi}_h$ coincides with $\tilde{\phi}$ except at large k.

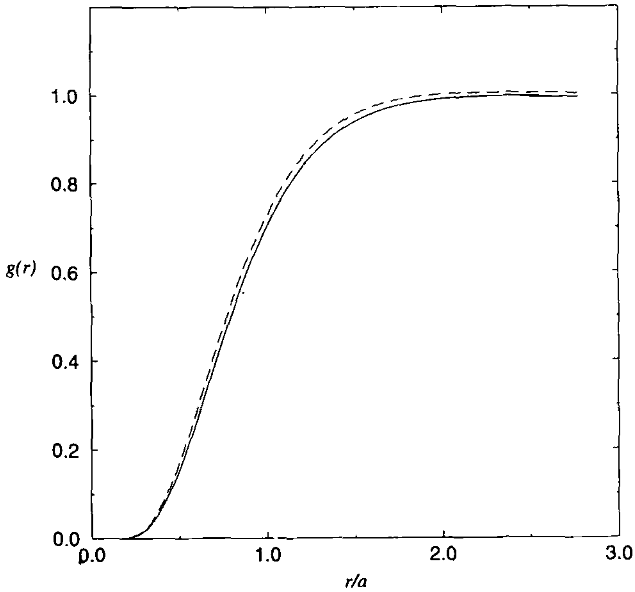

Fig. 5. The pair distribution function $g(r)$ for coupling constant $\Gamma = 1.7$ from the hypernetted chain approximation (dashed line) and from the density functional approximation (solid lines) after 20, 50, and 80 iterations. The latter three functions overlap. The radius is dimensionless, r/a, where $a = (3/4\pi n)^{1/3}$.

The set (77)–(81) was solved numerically by starting at the HNC solution for $c_2(r, n)$ and successively finding $\beta\mu_{ex}(n)$, $\omega(r)$, $v(r)$, $g(r, n)$, $c_2(r, n)$. Only functions corresponding to one density are iterated, and the quantities for effective densities different from the actual density are taken from HNC solutions. For $\Gamma < 0.1$, the end result was very close to the HNC input; for $\Gamma = 0.9$ and 1.7 (Figs. 4 and 5) there are only minor deviations. For $\Gamma \geqslant 2.6$ (Fig. 6) the above iteration scheme was not convergent, and the same is found for higher $\Gamma = 5.1$, 7.2, and 9.1. Note that the usage of HNC solutions at the effective densities limits the possibilities of finding solutions deviating from the HNC solution, and the conclusion is that the simple density functional does not have solutions agreeing well with HNC for $2 < \Gamma < 9$. In order to find solutions deviating from the HNC solutions, functions for a number of densities have to be iterated at the same time [see how the chemical potential from the HNC solution affects the pair dis-

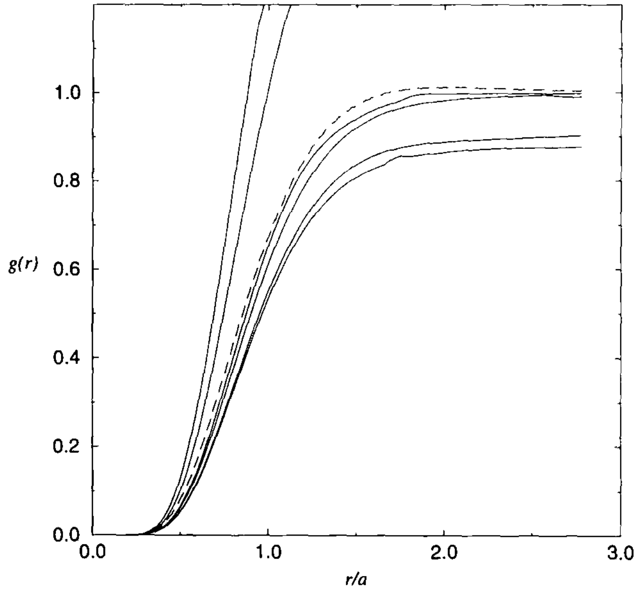

Fig. 6. The pair distribution function $g(r)$ for coupling constant $\Gamma = 2.6$ from the hypernetted chain approximation (dashed line) and from the density functional approximation (solid lines) after 1, 2, 5, 15, 20, and 30 iterations. The two solid lines closest to the HNC solution correspond to 1 and 2 iterations of the density functional approximation, and the deviation from the HNC solution grows with the number of the iteration (within the total number of iterations presented here). An example of nonconverging iterations.

tribution function in Eq. (77)]. Of greater interest is to try the density functional with a free energy expression (42), which requires substantial new numerical work, and will be reported in the future.

8. CONCLUSION

This paper has dealt with strategies for applying weighted density functional methods, with that of Curtin and Ashcroft as prototypical, to systems with Coulomb interactions. The approximation developed by Curtin and Ashcroft is based on an expression for the free energy, with the first- and second-order and a subset of higher-order correlation functions being retained "exactly." The drawback of the approximation (42) is the numerical difficulty with calculating the weight function, which after Fourier transformation is described by a differential equation (20). Several attempts have been made to find approximations which are more convenient to use but with similar properties. One alternative is to work directly with the profile equation, which makes the weight function simpler to calculate, but at the same time the resulting approximation (45) is less well motivated physically that the Curtin and Ashcroft approximation, since it is not derived from an exact free-energy expression. Several other simplified approximations of the same type can only be used for homogeneous systems, and are of less interest to us.(11, 14)

The two approximations described in Section 4 are applied to a two-dimensional, one-component plasma, with similar results. When writing the chemical potential for the two approximations, there is an extra term for the Curtin and Ashcroft approximation [compare (43) and (46)], which has a limited size for our test system. A more pronounced inhomogeneity is needed for assessment, and the simpler approximation is applied to a homogeneous three-dimensional, one-component plasma, where the inhomogeneity is given by regarding the potential around one particle as an external field. The calculation is carried out in such a way that only solutions close to the HNC solution can be found, which is the case for coupling constants $\Gamma < 2$. The results indicate that the simple density functional approximation does not give an accurate solution for higher coupling constants. There is reason to believe that the Curtin and Ashcroft-type approximation would give a better result,(15) but the numerical problems are not trivial, which is also documented in similar comparisons that have been performed by Denton and Ashcroft(16) and Brennan and Evans.(17) In both cases the interactions between particles are described by short-range potentials.

Further numerical tests of other types of density functional approximations have been performed by Kroll and Laird(18) for a hard-sphere fluid near a hard wall. However, the crucial case of Coulomb interaction has not been attended to as actively, and we suggest that the modifications studied in this paper are an effective entree into this field.

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