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# Exchange and correlation potentials for electron-ion systems at finite temperatures

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We have calculated the exchange and correlation corrections to the free energy ($F_{\text{xc}}$) and the chemical potential ($\mu_{\text{xc}}$) of an electron system at arbitrary degeneracies and temperatures. These are needed for density-functional, average-atom-type calculations of properties of plasmas and liquid metals. The problem of inverting the parametric relation between $\mu_{\text{xc}}$ and the density correction $n_{\text{xc}}$ is considered. We present easy-to-use analytic fits to $F_{\text{xc}}$ and $\mu_{\text{xc}}$ as functions of the temperature and density. We also consider the effect of a linearly responding ion background on the electron chemical potential as well as the ion chemical potential, as these are needed in calculations of ion-electron systems at arbitrary degeneracies and densities.

## I. INTRODUCTION

The objective of this paper is to provide some of the basic information on the exchange and correlation potentials and thermodynamic functions of an electron fluid, for densities and temperatures of the sort encountered in the study of strongly coupled plasmas and liquid metals.

Many problems in plasmas and liquid metals can be reduced to a theory[1] of an inhomogeneous electron fluid[2] coupled to an ion subsystem which can be described by a Gibbs-Boltzmann formulation. In the simpler approaches[3,4] the ionic system is replaced by a uniform background[5] or taken to be in its zero-temperature configuration defined by Wigner cells.[6] The electron subsystem is then treated using an effective single-particle Schrödinger equation or Thomas-Fermi-type equation. These equations contain an effective one-electron potential $V_e(r)$ made up of the usual one-body terms, the self-consistent Hartree potential, and also an effective potential $V_{\text{xc}}(r)$ which simulates the effects of exchange and correlation arising from the rest of the electrons. The rigorous formulation of this approach is found in density-functional theory[2] (DFT) which specifies $V_{\text{xc}}(r)$ to be a unique but unknown functional of the one-electron distribution $n(r)$. Similarly, exchange-correlation corrections to other thermodynamic functions can be introduced. As the exact functionals are unknown, they are usually evaluated in the local density approximation (LDA) where, for example, the exchange and correlation correction to the free energy $F_{\text{xc}}$ is taken to be

$$F_{\text{xc}}=\int n(r)f^{h}_{\text{xc}}[n(\vec{r})]d\vec{r}\,, \tag{1.1}$$

where $f^h_{\text{xc}}[n(r)]$ is the exchange-correlation correction per particle for the homogeneous electron system at a density $\bar{n}=n(r)$. Thus we see that the properties of the homogeneous electron system are of basic importance in the study of inhomogeneous systems.

The exchange-correlation potential $V_{\text{xc}}$ at any temperature[7] is found to be identical with $\mu_{\text{xc}}$ for uniform systems. The finite-temperature density-functional theory uses the grand canonical ensemble. For a given temperature $T$, volume $V$, and chemical potential $\mu$, the thermodynamic potential $\Omega$ is a minimum for the correct density distribution $n(r)$. In the homogeneous problem at density $\bar{n}$ we have

$$\Omega(T,V,\mu)=\Omega_0+\Omega_{\text{xc}}(T,V,\mu)\,, \tag{1.2}$$

where $\Omega_0$ is the value for the system without interactions. Once $\Omega_{\text{xc}}(T,V,\mu)$ is obtained, and then only, can we eliminate $\mu$ in favor of the density $\bar{n}$ via the parametric relation

$$N=\bar{n}V=-\left[\frac{\partial\Omega}{\partial\mu}\right]_{TV}. \tag{1.3}$$

If this inversion is not carried out and if $\Omega_{\text{xc}}(T,V,\mu)$ is simply treated as $\Omega_{\text{xc}}(T,V,\bar{n})$, where $\mu$ has been eliminated using zero-order theory, incorrect thermodynamic results will be obtained. Thus Gupta and Rajagopal[8] have reported tabulations of $\Omega_c$ for the ring sum, viz., $\Omega_r$, which are negative in sign and incorrect in magnitude although, as is well known, it should in the classical limit lead to the positive Debye-Hückel value of $\Omega_r/V=-P_r=e^2\bar{n}\lambda/6$, where $\lambda$ is the Debye screening constant. From the detailed discussion of their calculations given by Gupta and Rajagopal[9] [see Eqs. (104) and (105) of Ref. 9], it is clear that these authors[10] treat $\Omega(T,V,\mu)$ as if it were $\Omega(T,\mu,\bar{n})$, without going through the relation (1.3). Panat and Amritkar[11] have unfortunately followed the work of Gupta and Rajagopal[8] and reported tabulations of $\Omega_r$ which are really the Helmholtz free energy as in the case of Gupta and Rajagopal. In view of these confusions found in the recent literature, a reexamination of the problem is necessary.

In Sec. II we will briefly state the necessary theory for the calculation of $F_{\text{xc}}$ and $\mu_{\text{xc}}$, where the correlations will be treated via the random-phase approximation (RPA), also called the ring sum (or Montroll-Ward graphs). The passage from the grand canonical ensemble variable $\mu$ to the canonical ensemble variables $\bar{n}$, i.e., the density, will be restated. In Sec. III we present results for $f_{\rm xc}=F_{\rm xc}/\bar{n}$ and $\mu_{\rm xc}$ for a range of densities and temperatures in a convenient parametrized form. Here we make contact with some of the work of the East German group[12–15] and the earlier work of Pokrant[16] where alternative methods and approximations have been used. Finally, in Sec. IV we consider the effect of a responding ion background to linearly screen the electron-electron interactions and present results for these.

## II. REVIEW OF THE THEORY

A detailed discussion of the theory, both from the point of view of the self-energy and the grand potential $\Omega(T,V,\mu)$ is given in Ref. 7. Only a brief review is given here for completeness and to define the notation.

We define

$$\begin{aligned}\Omega(T,V,\mu)&=-T\ln Z\\ &=\Omega_0(T,V,\mu)+\Omega_{\rm xc}(T,V,\mu)\ ,\end{aligned}\tag{2.1}$$

where $Z$ is the partition function and $T$ the temperature in energy units. $\Omega_0(T,V,\mu)$ characterizes the noninteracting system. Its chemical potential $\mu=\mu_0$ is obtained from the equation (atomic units)

$$\bar{n}=2\sum n_k\ ,\quad n_k=1/(1+e^{\beta(\epsilon_k-\mu_0)})\ ,\tag{2.2}$$

where

$$\bar{n}=N/V\ ,\quad \beta=1/T\ ,\quad \epsilon_k=k^2/2\ .$$

This implicit relation for $\mu_0$ can be written as

$$\bar{n}=(\sqrt{2}/\pi^2)\beta^{-3/2}I_{1/2}(\beta\mu_0)\tag{2.3}$$

and then, using the resulting $\mu_0$, we have

$$\begin{aligned}\Omega_0/V=-P&=-2T\sum\ln(1+e^{\beta(\mu_0-\epsilon_k)})\\ &=(\sqrt{2}/\pi^2)\beta^{-5/2}\tfrac{2}{3}I_{3/2}(\beta\mu_0)\ .\end{aligned}\tag{2.4}$$

Here $I_\nu(z)$ is the Fermi integral defined by

$$I_\nu(z)=\int_0^\infty\frac{dx\,x^\nu}{e^{x-z}+1}\ ,\quad \nu\geq-\tfrac{1}{2}\ .$$

For future use we also define the electron sphere radius $r_s$ and the zero-temperature Fermi energy $E_F$ (atomic units) as

$$r_s=\left[\frac{3}{4\pi\bar{n}}\right]^{1/3}\ ,\quad 2E_F=k_F^2=\frac{1}{\alpha^2r_s^2}\ ,\quad \alpha=\left[\frac{4}{9\pi}\right]^{1/3}\ .\tag{2.5}$$

*Interacting system.* When we switch on the interactions, the change in $\Omega$, denoted by $\Omega_{xc}(T,V,\mu)$, can be calculated by diagrammatic perturbation theory. $\Omega_{\rm xc}$ consists of $\Omega_x$, which is the first-order term and is linear in the bare potential. $\Omega_c$ is the correlation term which by definition includes all other terms. If we consider the perturbation series as an expansion in powers of the *screened* Coulomb potential $\tilde{u}$, then the procedure used here may be regarded as a first-order calculation in the RPA-screened potential.

Thus we write

$$\Omega=\Omega_0(\mu)+\Omega_{\rm xc}^{(1)}(\mu)+(\cdots)\ ,\tag{2.6}$$

where the ellipsis represents higher order in $\tilde{u}$.

As seen from the work of Mermin (see Ref. 2), the exchange-correlation potential $V_{\rm xc}$ is the functional derivative of $\Omega_{\rm xc}$ with respect to the density. Hence, and for other purposes, it is desirable to eliminate $\mu$ in favor of the density $\bar{n}$, thus passing from the grand canonical ensemble to the canonical ensemble. This is achieved by the relation

$$\bar{n}=-\frac{1}{V}\left[\frac{\partial\Omega}{\partial\mu}\right]_{T,V}\tag{2.7}$$

noting that the physical density $\bar{n}$ is the density inclusive of corrections, viz.,

$$\bar{n}(\mu)=n^0(\mu)+n_{\rm xc}(\mu)\ ,\tag{2.8}$$

while the inversion is of the form

$$\mu(\bar{n})=\mu^0(\bar{n})+\mu_{\rm xc}(\bar{n})\ .\tag{2.9}$$

Now, given an $\Omega_{\rm xc}$ the inversion may be performed numerically to obtain $\mu_{\rm xc}(\bar{n})$, or alternatively, a linearized version of (2.9) may be considered, as in Ref. 7 [see Eqs. (4.16)–(4.18)]. The two procedures will *not* in general lead to equivalent results. We believe that the linearized inversion is more in keeping with our evaluation of $\Omega_{\rm xc}$ to first order in the RPA-screened potential. Thus

$$\mu=\mu_0+\mu_{\rm xc}^{(1)}\ .\tag{2.10}$$

$\mu_0$ is determined from a numerical inversion of

$$\bar{n}=\frac{\sqrt{2}}{\pi^2}\beta^{-3/2}I_{1/2}(\beta\mu_0)\ .$$

Then, expanding $\Omega(\mu)$ we have, as in Kohn and Luttinger[17] (see also Stolzmann and Kraeft[18]),

$$\begin{aligned}\mu_{\rm xc}^{(1)}&=-\frac{(\partial\Omega^{(1)}/\partial\mu)_{\mu=\mu_0}}{(\partial^2\Omega_0/\partial\mu^2)_{\mu=0}}\\ &=\frac{(\partial\Omega_{\rm xc}^{(1)}/\partial\mu)_{\mu=\mu_0}}{(\partial\bar{n}/\partial\mu)_{\mu=\mu_0}}\ .\end{aligned}\tag{2.11}$$

These results lead to the form

$$\Omega_{\rm xc}(\bar{n},T)=\Omega_{\rm xc}(\mu_0,T)-V\bar{n}\mu_{\rm xc}^{(1)}+(\cdots)\ ,$$

where the ellipsis represents higher-order terms. From the thermodynamic relation

$$\Omega=-PV=F-\bar{n}V\mu$$

we have

$$F_{\rm xc}(n,T)=\Omega_{\rm xc}(\mu_0,T)+(\cdots)\ ,\tag{2.12}$$

where the ellipsis represents higher terms,

$$\mu_{\rm xc}^{(1)}(n,T)=\frac{\partial\Omega_{\rm xc}(\mu_0,T)/\partial\mu_0}{\partial n(\mu_0,T)/\partial\mu_0}+\cdots\ ,\tag{2.13}$$

which is consistent with

$$\mu_{\mathrm{xc}}(n,T)=\frac{\delta F_{\mathrm{xc}}(n,T)}{\delta n} .$$

Equations (2.12) and (2.13) are the equations used in this work. Equation (2.13) also defines the exchange-correlation potential $V_{\mathrm{xc}}=\mu_{\mathrm{xc}}^{(1)}$ of DFT. The present analysis also shows that the $\Omega_r$ tabulated by Gupta and Rajagopal is really the ring-sum correction to the *Helmholtz free energy* $F_r$. Also, their $V_{\mathrm{xc}}$, which is also a calculation to first order in the screened potential, would prove to be the required $\mu_{\mathrm{xc}}$.

In the numerical calculation of $\Omega_{\mathrm{xc}}$ it is more convenient to deal with the part linear in the bare potential, viz., $\Omega_x$, separately from $\Omega_c$ which is just the ring sum in our approximation, as follows:

$$\begin{aligned}\Omega_x(\mu,T)/V&=-\sum_{\vec{q}}\sum_{\vec{k}}u_{\vec{k}-\vec{q}}n_q n_k\\&=\frac{1}{2\pi^3\beta^2}\int_{-\infty}^{\eta}[I_{-1/2}(x)]^2dx ,\end{aligned}\tag{2.14}$$

where

$$\eta=\beta\mu , \quad u_{\vec{k}-\vec{q}}=\frac{1}{V}\frac{4\pi}{|\vec{k}-\vec{q}|^2} .$$

The ring-sum contribution is

$$\begin{aligned}\Omega_c&\simeq\Omega_r(\mu,T)/V\\&=\sum_n\frac{1}{2\beta}\frac{1}{(2\pi)^3}\int d\vec{q}\{\ln[1-u_q\pi^0(q\nu_n)]\\&\qquad+u_q\pi^0(q\nu_n)\} ,\end{aligned}\tag{2.15}$$

where $\nu_n=2n\pi/\beta$ and $\pi^0(q,\nu_n)$ is the Lindhard function. For computational purposes we write this as

$$\begin{aligned}\Omega_r(\mu,T)/V=\frac{1}{\sqrt{2}\pi^2}\beta^{-5/2}\sum_n\int_0^{\infty}Q^2dQ\{\ln[1-X_n(Q)]\\+X_n(Q)\} ,\end{aligned}\tag{2.16}$$

$$X_n(Q)=-\frac{\sqrt{2}\beta}{\pi}\frac{1}{Q^3}F_n(Q,\eta) , \quad Q=q\sqrt{\beta/2}$$

with

$$F_n(Q,\eta)=\int_0^{\infty}\frac{x\,dx}{1+e^{x^2-\eta}}\ln\left[\frac{n^2\pi^2+Q^2(Q/2+x)^2}{n^2\pi^2+Q^2(Q/2-x)^2}\right] .$$

These equations provide an approximation to the perturbation series for $\Omega$ to first order in the screened Coulomb potential $\tilde{u}$. The range of validity of such an approximation is unknown but we believe that *it captures the most important part of the correlation corrections even for large* $r_s$. To qualify this more carefully, we note from the study of Vosko, Wilk, and Nusair[19] (their Table 5) that, for $T=0$, the maximum deviation of the RPA correlation energy from the Ceperley-Alder[20] Monte Carlo calculations is 13%, occurring at $r_s=15$. At $r_s=1$ and 100 they give deviations of 6% and 8%.

At very large $r_s$, one may consider the formation of a Wigner lattice.[21] In the simplest approximation the electrons can be considered to define a set of harmonic oscillators with vibration frequency $\omega_p/\sqrt{3}$, where $\omega_p$ is the plasma frequency. Thus, at finite temperatures, this picture is unlikely to hold unless

$$T\ll\omega_p=(3/r_s)^2 .$$

Also, for large $r_s$ since $E_F\propto 1/r_s^2$ we note that the electron system will rapidly approach the classical limit for which many results are available.[22]

## III. RESULTS FOR THE HOMOGENEOUS ELECTRON SYSTEM

In this section we present our results in the form of convenient analytic fits and compare them with existing calculations. It is convenient to parametrize $f_x=(F_x/N)$ and $\mu_x$ (i.e., $V_x$) separately from $f_c=(F_c/N)$ and $\mu_c$ (i.e., $V_c$), and then form $f_{\mathrm{xc}}$ and $\mu_{\mathrm{xc}}$. This is motivated by the fact that $f_x$ and $\mu_x$, being linear in the density, can be represented by a simple form independent of $r_s$ by a suitable choice of units, and also because $f_x$ and $f_c$ were calculated by two separate formulas for $\Omega_x$ and $\Omega_c$ [Eqs. (2.14) and (2.16)] although their sum formally represents the first-order dynamically screened exchange graph free of logarithmic divergencies at $T\rightarrow 0$ limit.[23,24]

The calculation of $f_c$ and $\mu_c$ needs some care to ensure that the $Q$ integration and the sum over $n$ given in Eq. (2.16) have converged. For $n\leq 20$ the sum was explicitly evaluated. For $21\leq n\leq 100$ a Padé approximant to $\int Q^2dQ[\ln(1-X_n)+X_n]$ based on the values for $n<21$ was used. For the range $n>100$ an integral was performed with an approximation of the form $F_n\rightarrow 4I_{1/2}(\eta)Q^3/(Q^4+aQ^2+4\omega^2)$.

A strong test of the quality of the numerical calculation can be obtained by noting that[23,24] the logarithmic divergence in $\Omega_x$ for $T\rightarrow 0$ (i.e., $\eta\rightarrow\infty$) is exactly canceled by a similar term in $\Omega_c$, so that $\Omega_{\mathrm{xc}}$ is completely well behaved. Horowitz and Thieberger[23] give

$$\Omega_X/V=-\frac{1}{2\pi^3\beta^2}\left[2\eta^2-\frac{\pi^2}{3}\ln\eta+\cdots+O(1/\eta^2)\right] ,$$

$$\eta\rightarrow\infty$$

where the ellipsis represents a constant.

Hence, by adding $\ln\eta/(6\pi\beta^2)$ to $\Omega_r/V$ we should find that the result is proportional to $T^2$ for small $T$. This was found to hold very accurately for sufficiently large $\eta$, (e.g., $\eta>10$ for $\mu=0.5$ a.u.) in all the cases examined. Calculations were carried out for $r_s=0.1$ to $r_s=5$ and the results have been parametrized as follows.

### A. Exchange contributions

We give the zero-temperature and high-temperature limits, viz.,

$$\mu_x(0) = -\frac{k_F}{\pi} = -0.6109/r_s \tag{3.1}$$

in a.u. Using the letter $h$ to imply the high-temperature limit,

$$\mu_x(h) = \mu_x(0)(2/3t) ,$$

where $t = T/E_F$. The following forms were found to reproduce the numerical data for $0.1 \le T/E_F \le 12$ quite accurately:

$$f_x(r_s t)/\mu_x(0) = \frac{0.75 + 3.04^3 63t^2 - 0.092\,270t^3 + 1.703\,50t^4}{1 + 8.310\,51t^2 + 5.1105t^4} \times \tanh(1/t) \tag{3.2}$$

and

$$\mu_x(r_s t)/\mu_x(0) = \frac{1.0 + 2.834\,31t^2 - 0.215\,120t^3 + 5.275\,86t^4}{1 + 3.943\,09t^2 + 7.913\,79t^4} \times \tanh(1/t) . \tag{3.3}$$

Note that we have used $\mu_x(0)$ as the unit of energy in both (3.2) and (3.3). Although $\mu_x(r_s t)$ can be obtained from (3.2) by differentiation, the independent parametrization given in (3.3) is more convenient.

Note that these parametrizations also provide a representation for $\Omega_x$ and the pressure $p_x (= -\Omega_x/V)$ via the standard thermodynamic relations

$$-p_x/\bar{n} = f_x - \mu_x . \tag{3.4}$$

The analytic forms given by Eqs. (3.2) and (3.3) deviate from the original tables by not more than 0.5% throughout the range of $t$ considered (see Table I).

### B. Ring contributions

At the zero-temperature limit, $f_c(r_s,0)$ becomes identical with the energy per particle, viz., $\epsilon_c(r_s,0)$. Vosko, Wilk, and Nusair[19] have given parametrization for $\mu_c(r_s,0)$ and $\epsilon_c(r_s,0)$ for $r_s$ up to 100. Thus

$$\epsilon_c(r_s,0) = A\left[\ln\frac{x^2}{X(x)} + \frac{2b}{Q}\tan^{-1}\frac{1}{2x+b} - \frac{bx_0}{X(x_0)}\frac{\ln(x-x_0)^2}{X(x)} + \frac{2(b+2x_0)}{Q}\tan^{-1}\frac{Q}{2x+G}\right] ,$$

where

$$x = \sqrt{r_s} , \quad X(x) = x^2 + bx + c , \quad Q = (4c-b)^{1/2} \tag{3.5}$$

with

$$x_0 = -0.409\,286 , \quad b = 13.0720 ,$$

$$c = 42.7198 , \quad A = 0.031\,907$$

in atomic units for RPA. The case including correlation beyond RPA is given as $x_0 = -0.104\,98$, $b = 3.727\,44$, $c = 12.9352$, with the same value of $A$ as before. The chemical potential is obtained from

$$\mu_c = \epsilon_c - \frac{A}{3}\frac{1+b_1 x}{1+b_1 x + b_2 x^2 + b_3 x^3} , \tag{3.6}$$

where, for RPA, $b_1 = 2.749\,273$, $b_2 = 0.771\,037$, and $b_3 = 0.057\,193$. However, for $0 < r_s < 6$ we can use the simpler form (for several parametrizations see MacDonald, Dharma-wardana, and Geldart[25])

$$\mu_c(r_s,0) = C\ln(1+1/y) ,$$

$$f_c(r_s,0) = C\left[(1+y^3)\ln(1+1/y) + \frac{y}{2} - y^2 - \frac{1}{3}\right] \tag{3.7}$$

with

$$C = 0.025\,45 , \quad y = r_s/19$$

for the correlation corrections in atomic units.

TABLE I. $f_x(t)$ and $\mu_x(t)$ are the first-order exchange contributions to the free energy per particle and the chemical potential. $t = T/E_F$, $\mu_x(0) = 0.610\,89/r_s$ (a.u.). The ring-sum contributions to $f_c(r_s t)$ and $\mu_s(r_s t)$ at $r_s = 1$ a.u. are also given, together with the values calculated from the analytic fitting formulas.

| $t = T/E_F$ | 0.1100 | 0.4973 | 0.9887 | 1.501 | 2.361 | 4.462 | 8.590 | 11.96 |
|---|---|---|---|---|---|---|---|---|
| $F_x(t)/\mu_x(0)$ | 0.7106 | 0.4587 | 0.2873 | 0.2031 | 0.1349 | 0.0733 | 0.0385 | 0.0278 |
| Eq. (3.2) | 0.7145 | 0.4571 | 0.2880 | 0.2034 | 0.1347 | 0.0732 | 0.0385 | 0.0277 |
| $\mu_x(t)/\mu_x(0)$ | 0.9899 | 0.7812 | 0.5331 | 0.3888 | 0.2633 | 0.1454 | 0.0769 | 0.0555 |
| Eq. (3.3) | 0.9866 | 0.7835 | 0.5310 | 0.3891 | 0.2646 | 0.1459 | 0.0769 | 0.0555 |
| $f_c(t)/\mu_x(0)$ | 0.1663 | 0.3474 | 0.4042 | 0.3984 | 0.3649 | 0.2968 | 0.2267 | 0.1955 |
| Eqs. (3.9) and (3.10) | 0.1657 | 0.3482 | 0.4059 | 0.3979 | 0.3658 | 0.2980 | 0.2264 | 0.1947 |
| $\mu_c(t)/\mu_x(0)$ | 0.1524 | 0.3272 | 0.4685 | 0.5060 | 0.4952 | 0.4236 | 0.3325 | 0.2888 |
| Eqs. (3.9)–(3.11) | 0.1511 | 0.3248 | 0.4688 | 0.5056 | 0.4955 | 0.4237 | 0.3303 | 0.2863 |

The classical-limit results at high temperatures (DeWitt,[22] also Ref. 12) have the form (atomic units)

$$f_c = -\tfrac{1}{3}\lambda_D + \frac{\sqrt{2\pi}}{32}\lambda_D^2 T^{-1/2} + \cdots ,$$
$$\mu_c = -\tfrac{1}{2}\lambda_D + \frac{\sqrt{2\pi}}{16}\lambda_D^2 T^{-1/2} + \cdots , \tag{3.8}$$

where

$$\lambda_D = (4\pi\bar{n}/T)^{1/2} .$$

Hence in the Debye-Hückel limit,

$$\mu_{\mathrm{DH}} = -0.638\,168(tr_s)^{-1/2}$$

in a.u.

The numerical results for $0.1 \leq r_s < 6$ and $0.1 \leq t \leq 12$ were found to be accurately representable by the following form (atomic units):

$$\phi_c(r_s t) = \phi_c(r_s,0)(1+c_1 t + c_2 t^{1/4})e^{-c_3/t} + \phi_c(r_s,h)e^{-c_4/t} , \tag{3.9}$$

where, when $\phi_c(r_s t) = f_c(r_s,t)$ we have $f_c(r_s,0)$ as given by Eqs. (3.7) or (3.5) and

$$f_c(r_s,h) = -0.425\,437(t/r_s)^{1/2}\tanh(1/t) . \tag{3.10}$$

Here $(r_s,h)$ implies the high-temperature representation

$$c_1 = \frac{10.900}{1+0.004\,72 r_s} ,$$
$$c_2 = \frac{39.5422 - 52.2381 r_s^{1/4} + 8.485\,54 r_s^{3/4}}{1+17.0999 r_s^{1/4}} ,$$
$$c_3 = \frac{3.888\,60}{1+0.133\,620 r_s^{1/2}} ,$$
$$c_4 = 0.122\,285 + 0.254\,281 r_s^{1/2} .$$

When $\phi_c(r_s,t) = \mu_c(r_s,t)$ we have $\mu_c(r_s,0)$ as given by (3.7) and (3.6) and

$$\mu_c(r_s,h) = -0.638\,168(t/r_s)^{1/2}\tanh(1/t) \tag{3.11}$$

and

$$c_1 = \frac{9.554\,32}{1+0.066\,66 r_s} ,$$
$$c_2 = \frac{3.579\,12 - 5.990\,65 r_s^{1/4} + 1.297\,22 r_s^{3/4}}{1+1.611\,26 r_s^{1/4}} ,$$
$$c_3 = \frac{4.802\,17}{1+0.423\,387 r_s^{1/2}} ,$$
$$c_4 = 0.293\,35 + 0.322\,565\sqrt{r_s} .$$

Illustrative results from these fitting formulas are given for the case $r_s = 1$ in Table I. The fitting formulas are sufficiently accurate for most calculations, but the original tabulations are available from the authors on request.

Richert and Ebeling[15] have recently proposed a Padé approximation form for $f_{\mathrm{xc}}$ and $\mu_{\mathrm{xc}}$ by making use of the analytic forms of $f_{\mathrm{xc}}$ and $\mu_{\mathrm{xc}}$ at the high-$T$ and low-$T$ limits. Their form has not been optimized by fitting to numerical calculations but is supported by having the correct limiting behaviors at high and low $T$. However, numerical tests at $r_s = 0.5$ using their form for RPA gave errors in excess of 25% for several temperatures.

It is of interest to compare our results with those of Pokrant[16] who has used completely different methods and given tabulations ($r_s = 0.5$—$3.39$) for $p_{\mathrm{xc}}/\bar{n}$ and $f_{\mathrm{xc}}$, and hence $\mu_{\mathrm{xc}} = f_{\mathrm{xc}} + p_{\mathrm{xc}}/\bar{n}$. Pokrant proceeds by evaluating the Slater sum using a finite temperature variational principle, together with a number of approximations typical of the statistical theory of fluids. His results for $T = 0$ are significantly different from those favored by Vosko *et al.* in their reevaluation of the available data inclusive of correlations beyond RPA. Figure 1 provides a comparison of our RPA data for $\mu_x$ and those of Pokrant which is presumed to contain correlation corrections beyond RPA.

## IV. EFFECT OF A RESPONDING ION BACKGROUND

In this section we examine the effect of ion-screening effects on $V_{\mathrm{xc}}$ $(=\mu_{\mathrm{xc}})$ and $f_{\mathrm{xc}}$ as this is of importance in density-functional calculations[1] of two-component (i.e., ions and electrons) systems. In this case we have to consider two correlation potentials, viz., $\mu_c^e$ and $\mu_c^i$, where the superscripts $e$ and $i$ denote electrons and ions.

Instead of (2.6) and (2.11) we have

$$\Omega(\mu^e,\mu^i,T) = \Omega_0^e(\mu_e,T) + \Omega_0^i(\mu^i,T) + \Omega_x(\mu^e,T) + \Omega_c(\mu^e,\mu^i,T) \tag{4.1}$$

and writing $s = i$ or $e$ we have

$$n_s = -\frac{\partial\Omega_0^s(\mu_0^s,T)}{\partial\mu_0^s} = -\frac{\partial\Omega(\mu^e,\mu^i,T)}{\partial\mu_0^s} , \tag{4.2}$$

$$\mu_c^s = \frac{\partial\Omega_c(\mu_0^s,\mu_0^{s'},T)}{\partial\mu_0^s} \Big/ \frac{\partial n_s}{\partial\mu_0^s} . \tag{4.3}$$

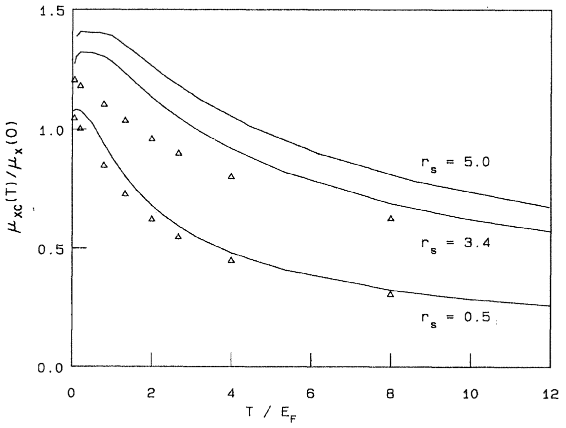

FIG. 1. Plots of $\mu_{\mathrm{xc}}(r_s,T)/\mu_x(0)$ for $r_s = 0.5$, 3.39, and 5.0. The triangles are from Pokrant's variational calculations (Ref. 16).

TABLE II. Comparison of calculations for a hydrogen plasma ($z=1,M=1848$) at $T=22.8$ eV. Ionic contributions to the ring sum are calculated using (a) the full Dawson function $D(Q/2\sqrt{M})$, (b) the small-$Q$ limit $Q/\sqrt{M}$.

| | | | | (a) | | | (b) | |
|---|---|---|---|---|---|---|---|---|
| $\eta^e$ | $T/E_F$ | $r_s$ | $-F_c/\bar{n}$ | $-\mu_c^e$ | $-\mu_c^i$ | $-F_c/\bar{n}$ | $-\mu_c^e$ | $-\mu_c^i$ |
| −4.0 | 11.995 | 5.124 | 0.1459 | 0.1037 | 0.1108 | 0.1460 | 0.1037 | 0.1110 |
| −3.0 | 6.183 | 3.685 | 0.2308 | 0.1579 | 0.1776 | 0.2310 | 0.1579 | 0.1780 |
| −2.0 | 3.235 | 2.665 | 0.3542 | 0.2255 | 0.2792 | 0.3548 | 0.2256 | 0.2803 |
| −1.0 | 1.740 | 1.955 | 0.5165 | 0.2892 | 0.4252 | 0.5178 | 0.2892 | 0.4279 |
| 0.0 | 0.989 | 1.474 | 0.7012 | 0.3199 | 0.6182 | 0.7043 | 0.3200 | 0.6244 |
| 1.0 | 0.611 | 1.158 | 0.8843 | 0.3091 | 0.8470 | 0.8908 | 0.3091 | 0.8598 |
| 2.0 | 0.414 | 0.953 | 1.0548 | 0.2794 | 1.0927 | 1.0663 | 0.2794 | 1.1155 |
| 4.0 | 0.237 | 0.722 | 1.3673 | 0.2332 | 1.5805 | 1.3936 | 0.2333 | 1.6323 |
| 7.0 | 0.140 | 0.555 | 1.7962 | 0.2085 | 2.2487 | 1.8529 | 0.2087 | 2.3605 |
| 10.0 | 0.099 | 0.467 | 2.1904 | 0.2012 | 2.8461 | 2.2847 | 0.2014 | 3.0318 |

In this paper we evaluate $\Omega_c(\mu^e,\mu^i,T)$ in the ring-sum (RPA) approximation. The new value of $V_c^e$ (i.e., $\mu_c^e$) will depend on the electron density $\bar{n}$ and the ion density $\bar{p}=\bar{n}/z$, where $z$ is the effective positive charge on the ions. The ion-correlation potential $\mu_c^i(\bar{n},\bar{p},T)$ evaluated in this manner would NOT be as good as the procedure based on the hypernetted-chain (HNC) integral equation given in Ref. 1 where nonlinear effects are also taken into account. However, $\mu_c^e(\bar{n},\bar{p},T)$, i.e., the correlation potential for electrons, will be superior to the form used in Ref. 1 since $\mu_c^e(\bar{n},\bar{p},T)$ includes (in linear response) the effects of the term denoted by $F_c^{ei}(n,p)$ which was neglected at that time.

Since the ions are classical at all temperatures of interest and much heavier than electrons, the RPA-response function $\pi^i(q,\nu_n)$ contributes only for the $n=0$ term. We have

$$\pi^i(q,\nu_0)=-\frac{1}{\pi^{3/2}}e^{\beta\mu^i}\frac{M^2}{\beta q}D\left[\frac{q}{2}\sqrt{\beta/2M}\right], \tag{4.4}$$

where $M$ is the ion mass and $D(x)$ is the Dawson function defined so as to have the limit $D(x\rightarrow 0)=2x$. Thus, when linear ion-screening effects are included in RPA in Eq. (2.16), we replace the $n=0$ term by

$$X_0(Q)=-\frac{\sqrt{2\beta}}{\pi}\frac{1}{Q^3}\left[F_0(Q,\eta^e)\right.$$
$$\left.+\sqrt{\pi}M^2z^2e^{\eta^i}D\left[\frac{Q}{2\sqrt{M}}\right]\right], \tag{4.5}$$
$$e^{\eta^i}=\left[\frac{\pi\beta}{M}\right]^{3/2}\sqrt{2}(\bar{n}/z)\,,\quad \eta^i=\beta\mu^i\,.$$

The nonzero-frequency contributions ($n\neq 0$) come only from the electrons. The small-$Q$ limit of $D(Q/2\sqrt{M})$ corresponds to the Debye-Hückel screening function. In Table II we present results for a typical temperature ($T=22.8$ eV) of a hydrogen plasma ($z=1$, $M=1848$) to examine the effect of $Q$ dispersion in the ion-response function. $Q$ dispersion is found to be relatively unimportant for $\mu_c^e$, but it has a significant effect on $\mu_c^i$.

To study the effect of softening of the ion background we define the ion-response factor $\zeta=(\lambda_D^i/\lambda_D^e)^2$, where $\lambda_D$ is the corresponding Debye screening constant. The rigid ion background corresponds to $\zeta=0$, while a responding proton gas corresponds to $\zeta=1$. The results of this calculation which exploits the small-$Q$ limit of the Dawson function are shown in Fig. 2.

In Table III we give results for $f_c$, $\mu_c^e$, and $\mu_c^i$ for a hydrogen plasma at $r_s=1$ with the ion-response factor $\zeta=0.5$ and 1.0, together with $f_c$ and $\mu_c^e$ for the system with a rigid-ionic background ($\zeta=0$). Figure 3 displays $\mu_c^e$ for other values of $r_s$ and as a function of temperature. Note that the effect of ion correlations is more important at small $r_s$ and near the region where $\mu$ changes sign ($T/E_F\approx 1.0$).

We have not attempted to parametrize $\mu_c^e(\bar{n},\zeta,T)$ or equivalently the $\mu_c^e(\bar{n},\bar{p},T)$ data as was done for the case of the uniform background. Tabulations are available from the authors if needed. However, a convenient ap-

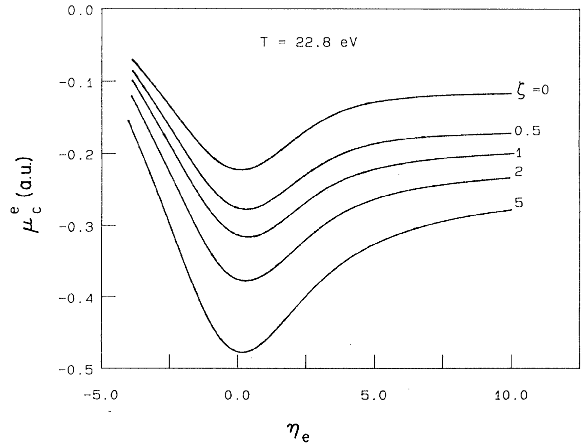

FIG. 2. Variation of $\mu_c^e$ (a.u.) for an electron-ion plasma at $T=22.8$ eV for different values of the ion-response factor $\zeta=(\lambda_D^i/\lambda_D^e)^2$, calculated using the small-$Q$ limit of the Dawson function. Here $\eta_e=\beta\mu_0^e$.

TABLE III. Correlation correction $f_c$, $\mu_c^e$, and $\mu_c^i$ in atomic units for a hydrogen plasma at $r_s=1$ with the ion-response factor $\zeta=0$, 0.5, and 1, with $\zeta=(\lambda_{\rm DH}^i/\lambda_{\rm DH}^e)^2$. The case $\zeta=0$ corresponds to a rigid-ion background for which $\mu_c^i\equiv0$.

| | | $-f_c$ | | | $-\mu_c^e$ | | $-\mu_c^i$ | |
|---|---|---|---|---|---|---|---|---|
| $T/E_F$ | 0.0 | 0.5 | 1.0 | 0.0 | 0.5 | 1.0 | 0.5 | 1.0 |
| 0.110 | 0.1016 | 0.6078 | 1.4007 | 0.0931 | 0.1279 | 0.1438 | 0.3363 | 1.8012 |
| 0.4973 | 0.2122 | 0.5481 | 0.9965 | 0.1999 | 0.2613 | 0.3032 | 0.1985 | 0.9931 |
| 0.9887 | 0.2469 | 0.5246 | 0.8746 | 0.2862 | 0.3561 | 0.4086 | 0.1582 | 0.7639 |
| 1.5009 | 0.2434 | 0.4860 | 0.7852 | 0.3091 | 0.3797 | 0.4346 | 0.1364 | 0.6486 |
| 2.3607 | 0.2229 | 0.4285 | 0.6779 | 0.3025 | 0.3696 | 0.4231 | 0.1144 | 0.5381 |
| 3.2348 | 0.2030 | 0.3839 | 0.6019 | 0.2838 | 0.3463 | 0.3969 | 0.1003 | 0.4692 |
| 4.4623 | 0.1813 | 0.3392 | 0.5283 | 0.2588 | 0.3156 | 0.3621 | 0.0872 | 0.4064 |
| 6.1826 | 0.1595 | 0.2964 | 0.4596 | 0.2312 | 0.2817 | 0.3234 | 0.0754 | 0.3501 |
| 8.5899 | 0.1385 | 0.2564 | 0.3965 | 0.2031 | 0.2475 | 0.2843 | 0.0648 | 0.3003 |
| 11.955 | 0.1194 | 0.2205 | 0.3406 | 0.1764 | 0.2153 | 0.2476 | 0.0556 | 0.2572 |

proximate analytic form which describes the effect of the responding ion background on $\mu_c^e$ can be obtained by exploiting the fact that (i) only the $n=0$ term in the frequency sum for $\Omega_r$ is involved, (ii) the $Q$ dispersion in the Dawson function is not too important for $\mu_c^e$.

We separate out the $n=0$ term in the ring sum and write

$$\begin{aligned}\Omega_r(\mu^e,\mu^i,T)&=\Omega_r(n\neq0)+\Omega_r(n=0)\\&=\Omega_r(n\neq0)+\Omega_r^e(n=0)\\&\quad+[\Omega_r(n=0)-\Omega_r^e(n=0)]\ .\end{aligned}\tag{4.6}$$

Here $\Omega_r^e(n=0)$ is the static term in the electron-gas ring-sum calculation with the rigid uniform ionic background. Hence we rewrite (4.6) as

$$\Omega_r(\mu^e,\mu^i,T)=\Omega_r^e(\mu^e,T)+\Delta\Omega_r(n=0)\ ,\tag{4.7}$$

where $\Omega_r^e(\mu^e,T)$ is the *total* electron-gas ring sum while $\Delta\Omega_r(n=0)$ is the correction to the $n=0$ term arising from the presence of ion screening. We evaluate $\Delta\Omega_r(n=0)$ in the $q\to0$ approximation as follows:

$$\Delta\Omega_r(n=0)=\Omega_r(n=0,\mu^e,\mu^i)-\Omega_r^e(n=0,\mu^e)\ ,\tag{4.8}$$

$$\Omega_r(n=0,\mu^e,\mu^i)\simeq\frac{T}{4\pi^2}\int_0^\infty\left[\ln\left[1+\frac{\lambda_T^2}{q^2}\right]-\frac{\lambda_T^2}{q^2}\right]q^2dq\ ,$$

$$\Omega_r^e(n=0,\mu^e)\simeq\frac{T}{4\pi^2}\int_0^\infty\left[\ln\left[1+\frac{\lambda_e^2}{q^2}\right]-\frac{\lambda_e^2}{q^2}\right]q^2dq\ .\tag{4.9}$$

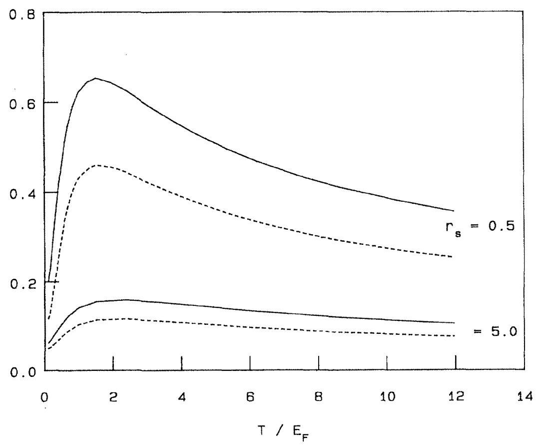

FIG. 3. $V_c^e$ (i.e., $\mu_c^e$) for $\zeta=1$ (solid curves) at $r_s=0.5$ and 5.0. The data for a rigid-ion background $\zeta=0$ are also given (dashed curves) for $r_s=0.5$ and 5.0 (atomic units).

Here $\lambda_T$ is the total (electron plus ion) screening constant, while $\lambda_e$ is the screening constant for the electrons only.

Doing the integrations in (4.8) and eliminating the $\mu$ variable in favor of the density, we have, in an obvious notation,

$$\Delta F_c(n=0,\bar n,\bar p,T)=-\frac{T}{12\pi}(\lambda_T^3-\lambda_e^3)\ ,\tag{4.10}$$

where

$$\lambda_e^2=\frac{2}{\pi}\sqrt{2T}I_{-1/2}(\beta\mu_0^e)$$

and

$$\lambda_T^2=4\pi\bar n\beta z+\lambda_e^2$$

since

$$\bar p=\bar n/z\ .$$

Hence

$$\begin{aligned}\Delta\mu_c^e(n=0,\bar n,\bar p,T)&=\frac{\partial}{\partial\bar n}\Delta F_c(n=0,\bar n,\bar p)\\&=\frac{T}{4\pi}(\lambda_T^2\lambda_T'-\lambda_e^2\lambda_e')\ .\end{aligned}\tag{4.11}$$

Equation (4.10) can be easily evaluated since it involves only standard Fermi integrals and a derivative with respect to the density $\bar n$ [denoted by primes on $\lambda$ in Eq. (4.11)]. Once $\Delta\mu_c^e$ is calculated, the total $\mu_c^e(\bar n,\bar p,T)$ can be written as

$$\mu_c^e(\bar n,\bar p,T)=\mu_c^e(\bar n,T)+\Delta\mu_c^e(n=0,\bar n,\bar p,T)\ .\tag{4.12}$$

$\mu_c^e(\bar{n},T)$ needed here may be calculated from the parametrization given in Eq. (3.10). Hence $\mu_c^e(\bar{n},\zeta,T)$ may be approximately evaluated by this procedure which is computationally quite straightforward. The same calculation can be adopted for $f_c$ via Eq. (4.10).

## V. CONCLUSIONS

We have presented convenient and adequately accurate parametrizations of the exchange and correlation corrections to the free energy and the chemical potential needed in density-functional calculations of strongly coupled electron-ion systems at arbitrary degeneracies. In addition to the detailed calculation, a simple method of calculating the properties of electron-ion systems by an approximation to the zero-frequency term in the expression for the ring sum is also presented. Although we have presented correlation corrections to the ion chemical potential ($\mu_c^i$), it is not recommended that they be used in strong coupling situations since the procedure given in Ref. 1, based on the HNC equation, is superior to the present (linear-response) approach. By contrast, $\mu_c^e(\bar{n},\bar{\rho},T)$ presented here will be very useful in future DFT calculations of systems with electrons and ions.

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