MANY-BODY PERTURBATION THEORY FOR THE PRESSURE OF AN ELECTRON-ION SYSTEM

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I. INTRODUCTION AND SUMMARY

For a long time, the mainstay [1,2] of the theory of the equation of state at higher temperatures and densities has been the Thomas-Fermi or the Thomas-Fermi-Dirac theory. These theories correctly reduce to the electron ideal gas [3] at sufficiently high temperature, but as we [4] pointed out previously, even the first deviation from this limit is incorrectly given by these theories. Our interest in this paper is to investigate the quality of these approximate theories in light of some of the results of modern quantum many-body theory. In the second section, we derive from quantum, many-body theory by means of finite-temperature (Matsubara) perturbation theory the corrections to this limit through order e^4, where e is the electronic charge. These coefficients are functions of the de Broglie density (3.2) alone. In the third section, we obtain easily computable representations of these coefficients which are accurate to at least one-tenth of one percent. This accuracy is sufficient for our purposes. In the final section, we adapt an accurate representation of the Thomas-Fermi pressure (which we [5] have used previously) to incorporate the new coefficient information which we have now obtained. We find that double-digit percentage differences result in the pressures of quantum theory and Thomas-Fermi theory.

II. PERTURBATION THEORY

One goal in this paper is to compute, for general de Broglie density, the perturbations to the ideal Fermi gas pressure caused by the electrostatic interactions between electrons and ions. We will treat the electrons as Fermions, but will treat the ions as Maxwell-Boltzmann particles. The treatment of the ions could be improved, if required. The pressure we will be concerned with is actually the total pressure minus the ideal gas pressure of the ions. We start with the electrically neutral Hamiltonian,

$$H = \sum_{i=1}^{ZN} \frac{p_i^2}{2m} + \sum_{j=1}^{N} \frac{P_j^2}{2M} + \sum_{i<j}^{ZN} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} - \sum_{i}^{ZN} \sum_{j}^{N} \frac{Ze^2}{|\vec{r}_i - \vec{R}_j|} + \sum_{i<j}^{N} \frac{Z^2 e^2}{|\vec{R}_i - \vec{R}_j|}, \quad (2.1)$$

where $\vec{r}$, $\vec{p}$ are the position and momentum for the electrons and $\vec{R}$, $\vec{P}$ are for the

ions of charge Z. To treat our problem we employ finite-temperature perturbation theory (Matsubara [6]). It is known that when this theory is applied to the Coulomb potential, that some of the terms diverge in a rather serious manner. Gell-Mann and Brueckner [7] however have shown that if all the so-called "ring-diagrams" are summed up before the integration of the momentum transfer is performed, then the result is finite, but the order in the coupling constant e^2 is changed. We will discuss this point in more detail below. Bedenov [8] briefly describes his investigation of our case for a degenerate plasma. A fuller description is given by Abrikosov *et al.* [9]

To begin we note that the thermodynamic potential $p\Omega$, where p is the pressure and Ω is the volume, (See, for example, pp. 68-71 and 105-107 of Landau and Lifshitz [10]) is given by $-kT\log\mathcal{Z}$ where k is Boltzmann's constant, T is the absolute temperature and $\mathcal{Z}$ is the partition function from the grand canonical ensemble. In terms of other thermodynamic quantities $p\Omega = TS + \mu N - U$, where S is the entropy, μ is the Gibbs free energy, or thermodynamic potential, per particle, N is the number of particles, and U is the internal energy. The perturbation series for the pressure is related to that for the energy by the observation that,

$$\frac{\partial(-kT\log\mathcal{Z})}{\partial e^2} = e^{-2}\langle V\rangle, \tag{2.2}$$

where V is the interaction potential, *i.e.* everything proportional to e^2 in (2.1). Thus,

$$p\Omega = \int_0^{e^2} e^{-2}\langle V\rangle\, de^2 + p_0\Omega, \tag{2.3}$$

relates the series for the energy and that for the pressure. Note that, of course, the wave function changes as e increases in the integral.

The finite-temperature perturbation series is conveniently described in the wave-number space representation. The wave-number representation for the interaction potential is

$$V(\vec{r}) = \frac{e^2}{r} \mapsto \tilde{v}(\vec{q}) = \frac{4\pi e^2}{q^2}. \tag{2.4}$$

The rules for the perturbation series for the interaction energy which insure that the proper quantum mechanical expectation values are taken are briefly: First draw the Goldstone type diagrams which are associated with the various terms in the perturbation series. We in fact use the type of diagrams discussed by Baker [11]. Here there are no lines entering on the left nor leaving on the right. Label every line in such a way that the wave-number is conserved at every vertex. Associate a frequency with each independent wave-number. The frequencies must also obey a conservation rule at every vertex. The frequencies on every Fermion line are odd ($\omega_n = (2n+1)\pi kT$) and those with every Boson line must be even ($\omega_n = 2\pi nkT$). Now with each fermion line (particle or hole) associate a factor of

$$\frac{e^{i\omega_n'\tau}}{i\omega_n' - \epsilon(\vec{p}\,') + \mu}, \tag{2.5}$$

where ω_n' and $\vec{p}\,'$ are the frequency and the wave-number associated with that line. We define,

$$\epsilon(\vec{p}) \equiv \frac{\hbar^2 p^2}{2m}, \tag{2.6}$$

where $\hbar$ is Planck's constant h divided by 2π. With each Boson line (the wavy lines internal to each interaction symbol) associate a factor of $\tilde{v}(\vec{q})$ where $\vec{q}$ is the wave-number associated with that line. Note that if the vertex is not electron-electron,

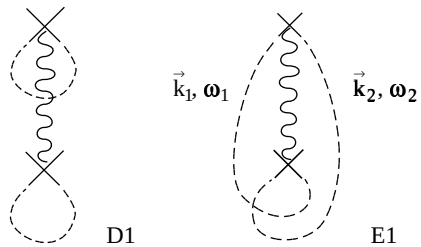

Fig. 1. The diagrams for the first-order interaction in e^2.

then a factor of Z or Z^2 would also be need as the case may be, and as it is really momentum that is conserved, account of the masses must be taken. Next examine the diagram of order n vertices and count the number of hole lines h and the closed loops l made by the combination of the particle and hole lines. Multiply the term by a factor of

$$\frac{(2s+1)^l(-1)^{h-l}(-kT)^{n+1}}{(2\pi)^{3(n+1)}2^n}. \tag{2.7}$$

Next sum over the independent frequencies, take the limit as $\tau \to 0$, and finally integrate over all the independent wave-numbers. The following identities are useful in doing the frequency sums.

$$\begin{aligned} kT\sum_{n=-\infty}^{+\infty}\frac{1}{2n\pi ikT+X} &= \frac{1}{2}\coth\left(\frac{X}{2KT}\right), \\ \lim_{\tau\to 0} kT\sum_{n=-\infty}^{+\infty}\frac{e^{i\tau}}{(2n+1)\pi ikT+X} &= \frac{1}{2}\tanh\left(\frac{X}{2kT}\right)+\frac{1}{2}\mathrm{sgn}(\tau), \\ n(\vec{p}) = \frac{1}{\exp\{[\epsilon(\vec{p})-\mu]/(kT)\}+1} &= \frac{1}{2}\left[1-\tanh\left(\frac{\epsilon(\vec{p})}{2kT}\right)\right]. \end{aligned} \tag{2.8}$$

Our goal will be to compute the corrections to the pressure to the order of e^4. The first step is to examine all the diagrams up to and including two interactions. We will, following Abrikosov *et al.* [9], ignore the ion exchange terms as relatively small. The electron-ion exchange terms do not exist as they are not identical particles. In first order in e^2, the direct terms, $D1$ shown in Fig 1, cancel as among the electron-electron, electron-ion and ion-ion terms by electrical neutrality. The first exchange term, $E1$ shown in Fig. 1, by our rules, gives the contribution,

$$p_{E1} = -\frac{4\pi e^2}{(2\pi)^6}\int\frac{d\vec{k}_1\,d\vec{k}_2}{(\vec{k}_1-\vec{k}_2)^2}n(\vec{k}_1)n(\vec{k}_2), \tag{2.9}$$

which agrees with the results of Abrikosov *et al.* [9], but is $\frac{3}{2}$ times that of the Thomas-Fermi-Dirac approximation of Cowan and Ashkin [2]. In the difference, the factor of two comes from Cowan and Ashkin's over counting of the number of exchange terms, and the factor of three comes from their use of the viral theorem, which is valid for the Thomas-Fermi model [1]. This result concludes the study of the first-order perturbation theory.

In second order in e^2 there are a number of cases to consider. The first is the so called direct term, $D2$, Fig. 2. We work initially, for ease of exposition, with the electron-electron terms. Since there are two equivalent direct terms, we get,

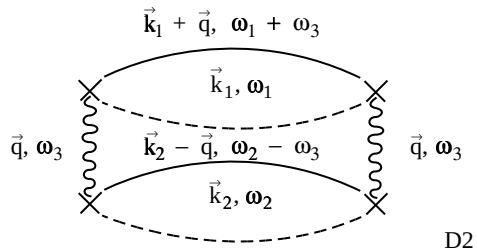

Fig. 2. The second-order direct-interaction diagram.

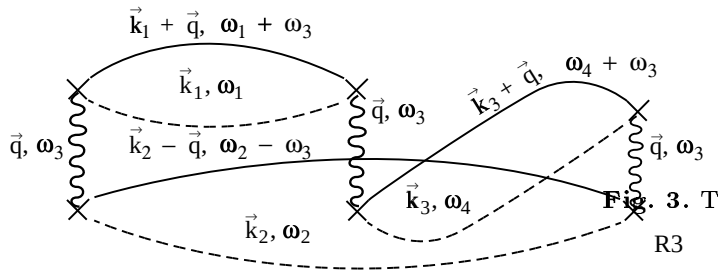

Fig. 3. The third-order ring diagram.

$$-\frac{2(4\pi e^2)^2(kT)^3}{(2\pi)^9}\sum_{\omega_1,\omega_2,\omega_3}\int\frac{d\vec{k}_1\,d\vec{k}_2\,d\vec{q}}{q^2q^2}\left[\frac{1}{i\omega_1-\epsilon(\vec{k}_1)+\mu}\frac{1}{i\omega_2-\epsilon(\vec{k}_2)+\mu}\right.$$
$$\left.\times\frac{1}{i\omega_1+i\omega_3-\epsilon(\vec{k}_1+\vec{q})+\mu}\frac{1}{i\omega_2-i\omega_3-\epsilon(\vec{k}_2-\vec{q})+\mu}\right], \tag{2.10}$$

where ω_1 and ω_2 are odd and ω_3 is even. The thing to notice is that the integral over $\vec{q}$ diverges as $q \to 0$. The solution to this problem was given by Gell-Mann and Brueckner [7] in the context of the ground-state energy problem. It is to sum up all the "ring diagrams" before doing the integral over the momentum transfer, $\vec{q}$. The Fourier transform trick used by them to sum up these diagrams to all orders is basically incorporated in our formalism, if we are careful to wait until after summing up all orders to sum over ω_3. Doing the sums over ω_1 and ω_2 in (2.10) we get,

$$-\frac{kT}{2(2\pi)^3}\sum_{\omega_3}\int d\vec{q}\left[\frac{8\pi e^2}{q^2}\Xi(\vec{q},\omega_3)\right]^2, \tag{2.11}$$

where

$$\Xi(\vec{q},\omega_3)=\frac{1}{(2\pi)^3}\int\frac{[n(\vec{k})-n(\vec{k}-\vec{q})]\,d\vec{k}}{-i\omega_3+\epsilon(\vec{k})-\epsilon(\vec{k}-\vec{q})}. \tag{2.12}$$

In third order in e^2 there is just one term, Fig. 3, which gives the contribution

$$-\frac{kT}{2(2\pi)^3}\sum_{\omega_3}\int d\vec{q}\left\{-\left[\frac{8\pi e^2}{q^2}\Xi(\vec{q},\omega_3)\right]^3\right\}, \tag{2.13}$$

In higher-orders, there are many "vertex orders" of the same diagram, but by the arguments of Gell-Mann and Brueckner [7], they are represented in our formalism by a

single term. The whole series of these most highly divergent terms in the perturbation expansion for $\langle V \rangle$ then formally sums to

$$-\frac{kT}{2(2\pi)^3}\sum_{\omega_3}\int d\vec{q}\left\{\frac{\left[8\pi e^2\Xi(\vec{q},\omega_3)\right]^2}{q^2+8\pi e^2\Xi(\vec{q},\omega_3)}\right\}. \tag{2.14}$$

When we convert (2.14) to the series for the $p\Omega$, by (2.3), we get, interchange the orders of integration,

$$-\frac{kT}{2(2\pi)^3}\sum_{\omega_3}\int d\vec{q}\left\{\ln\left[1+\frac{8\pi e^2}{q^2}\Xi(\vec{q},\omega_3)\right]-\frac{8\pi e^2}{q^2}\Xi(\vec{q},\omega_3)\right\}. \tag{2.15}$$

The next problem is to analyze the leading order behavior in the limit of small e^2. To this end we introduce the dimensionless variable,

$$y^2=\frac{Ze^2}{kTr_b},\quad \Omega=\tfrac{4}{3}\pi r_b^3 N. \tag{2.16}$$

If we re-express the wave number $\vec{q}=y\vec{p}$, then Ξ becomes,

$$\Xi(y\vec{p},\omega_3)=\frac{1}{(2\pi)^3}\int\frac{d\vec{k}\,\left(\frac{\Delta\epsilon}{4kT}\right)\operatorname{sech}^2\left(\frac{\epsilon(\vec{k})-\mu}{2kT}\right)+O(y^3)}{-i\omega_3+\Delta\epsilon}, \tag{2.17}$$

where

$$\Delta\epsilon=\hbar^2(2y\vec{p}\cdot\vec{k}-y^2p^2)/(2m), \tag{2.18}$$

and one term in (2.17) of nominal order y^2 is not shown because it vanishes on integration over the angles of $\vec{k}$. In order to do the sum over ω_3, there are two cases to consider. In the first, $\omega_3=0$, and

$$\Xi(y\vec{p},0)=\frac{1}{4kT(2\pi)^3}\int d\vec{k}\operatorname{sech}^2\left(\frac{\epsilon(\vec{k})-\mu}{2kT}\right), \tag{2.19}$$

which is independent of $\vec{p}$. In the case where $\omega_3\neq 0$, Ξ is of nominal order y which is already small compared to the $\omega_3=0$ case which was of order unity, but again the integration over the angles of $\vec{k}$ reduces the size even further to the order of y^2. Thus we only need to retain the $\omega_3=0$ term to give the leading order, plus the next order as well, for the sum of these ring diagrams. When we recognize that integration by parts *etc.* yields,

$$\int_0^\infty\left[\ln\left(1+\frac{1}{k^2}\right)-\frac{1}{k^2}\right]k^2\,dk=-\frac{\pi}{3}, \tag{2.20}$$

we may write that our sum of ring diagrams is

$$-\frac{kT}{(2\pi)^2}\left(\frac{\pi}{3}\right)\left[\frac{e^2}{(2\pi)^2kT}\int d\vec{k}\operatorname{sech}^2\left(\frac{\epsilon(\vec{k})-\mu}{2kT}\right)\right]^{3/2}, \tag{2.21}$$

which is of order e^3 with an error term of order e^5. The divergence in the integration over $\vec{q}$ has been converted into a lower order in the expansion parameter.

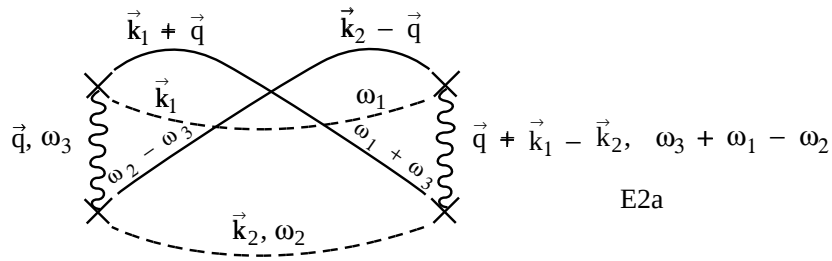

Fig. 4. The second-order exchange-interaction diagram.

The work to include the ion terms is just the same, except that e^2 is multiplied by $-Z$ for the electron-ion interactions and by Z^2 for the ion-ion interactions, the ions are being treated as spinless, and the ions have a Maxwell-Boltzmann distribution rather than a Fermi-Dirac one. The proper change is to make Ξ the sum of the electron (2.12), plus Z^2 times the ion function, which substitutes,

$$n_{\text{ion}}(\vec{k}) = \frac{1}{2}\exp\{[\mu - \epsilon(\vec{k})]/(kT)\}, \tag{2.22}$$

for $n(\vec{k})$. The factor $\frac{1}{2}$ is to take account of no ion spin. Thus (2.21) becomes, to take account of all the interactions,

$$p_{DH} = -\frac{kT}{(2\pi)^2}\left(\frac{\pi}{3}\right)\left[\frac{4\pi Z^2 N e^2}{kT\Omega} + \frac{e^2}{(2\pi)^2 kT}\int d\vec{k}\,\text{sech}^2\left(\frac{\epsilon(\vec{k})-\mu}{2kT}\right)\right]^{3/2}, \tag{2.23}$$

since the integral over the resulting function in the ion case is easily expressed in terms of the density normalization. This finishes the study of the terms of order e^3, or the Debye-Hückel term.

We now consider the calculation of the terms of order e^4 which we call the second exchange correction. We do not know of previous work on this term. The first contribution $E2a$ is the exchange, Fig. 4, of the the direct term shown in Fig. 2. Following of rules as expounded above, we obtain for electron-electron exchange, by reducing the integrand to dimensionless form,

$$\begin{aligned} p_{E2a} = {} & \frac{(4\pi e^2)^2}{2^5 kT(2\pi)^9}\left(\frac{2mkT}{\hbar^2}\right)^{5/2}\int \frac{d\vec{k}_1\,d\vec{k}_2\,d\vec{q}}{q^2(\vec{q}+\vec{k}_1-\vec{k}_2)^2}\frac{\sinh(\vec{q}\cdot(\vec{q}+\vec{k}_1-\vec{k}_2))}{\vec{q}\cdot(\vec{q}+\vec{k}_1-\vec{k}_2)} \\ & \times\left[\cosh\left(\frac{(\vec{q}+\vec{k}_1)^2}{2}-\frac{\mu}{2kT}\right)\cosh\left(\frac{k_1^2}{2}-\frac{\mu}{2kT}\right)\cosh\left(\frac{(\vec{k}_2-\vec{q})^2}{2}-\frac{\mu}{2kT}\right)\right. \\ & \left.\times\cosh\left(\frac{k_2^2}{2}-\frac{\mu}{2kT}\right)\right]^{-1} \end{aligned} \tag{2.24}$$

where use has been made of the standard identities,

$$\coth x + \coth y = \frac{\sinh(x+y)}{\sinh x \sinh y}, \quad \tanh x + \tanh y = \frac{\sinh(x+y)}{\cosh x \cosh y}, \tag{2.25}$$

to obtain this form.

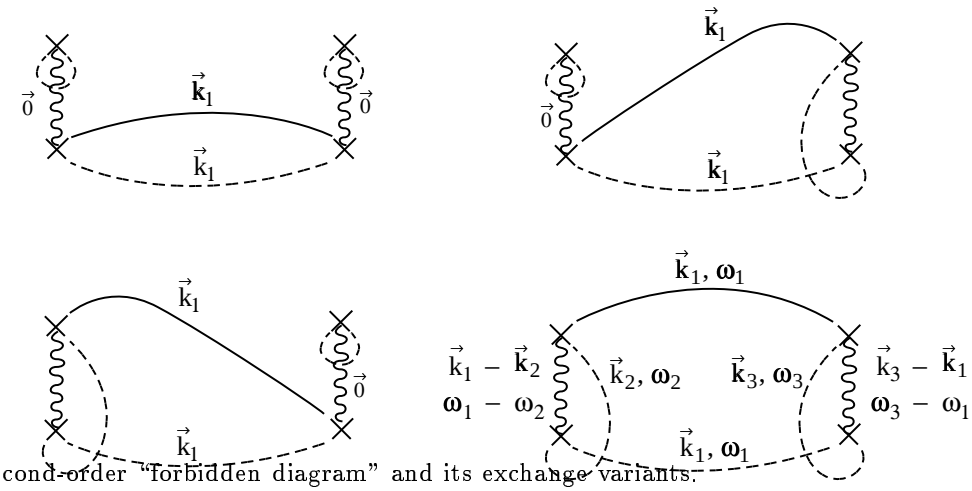

Fig. 5. The second-order "forbidden diagram" and its exchange variants.

E2b

Finally, there occurs to this order in perturbation theory one term which does not occur in the ground state energy expansion, plus its three exchange variants. They are shown in Fig. 5. The reason that they do not appear in the ground state energy perturbation theory is that, contrary to finite-temperature perturbation theory, in that theory there can not be simultaneously a hole and a particle with the same momentum. In finite-temperature theory, we are dealing with an ensemble and hence can have, on the average, fractional occupation of a state, and hence this case is not forbidden. In the first three terms shown in Fig. 5 is at least one interaction in which zero momentum is exchanged. All three of these cases cancel among the corresponding electron-electron, eletron-ion and ion-ion terms by electrical neutrality. In the final case, whose contribution we call $E2b$, there is exchange at both vertices. The contribution here for electron-electron exchange can be worked out by taking the $\partial/\partial X$ of the second identity of (2.8) to get the frequency sum where one of the denominators appears squared. Again reducing the integrand to dimensionless form, we obtain,

$$p_{E2b} = \frac{(4\pi e^2)^2}{2^3 kT(2\pi)^9}\left(\frac{2mkT}{\hbar^2}\right)^{5/2}\int \frac{d\vec{k}_1\, d\vec{k}_2\, d\vec{k}_3}{(\vec{k}_2-\vec{k}_1)^2(\vec{k}_1-\vec{k}_3)^2} \times \frac{\operatorname{sech}^2\left(\frac{1}{2}k_1^2 - \frac{\mu}{2kT}\right)}{\left[1+\exp\left(k_2^2-\frac{\mu}{kT}\right)\right]\left[1+\exp\left(k_3^2-\frac{\mu}{kT}\right)\right]}. \tag{2.26}$$

Again, as in the first exchange correction, we ignore here, and in $E2a$, the ion-ion exchange as being relatively small.

III. FUGACITY EXPANSION OF THE COEFFICIENTS.

In order to express the results of the previous section in an organized manner, we may write the pressure (total pressure minus the ideal gas pressure of the ions), to the order we have obtained it as,

$$\frac{p\Omega}{ZNkT} = g_0(\zeta) + g_1(\zeta)y + g_2(\zeta)y^2 + g_3(\zeta)y^3 + g_4(\zeta)y^4 + \cdots, \tag{3.1}$$

where y is given by (2.16), the de Broglie density is,

$$\zeta = \frac{ZN}{2\Omega}\left(\frac{h^2}{2\pi mkT}\right)^{\frac{3}{2}}, \tag{3.2}$$

and

$$
\begin{aligned}
g_1(\zeta) &= 0, \\
g_2(\zeta) &= \frac{\Omega r_b}{Z^2 N e^2} p_{E1}, \\
g_3(\zeta) &= \frac{\Omega r_b^{\frac{3}{2}} (kT)^{\frac{1}{2}}}{Z^{\frac{5}{2}} N e^3} p_{DH}, \\
g_4(\zeta) &= \frac{\Omega r_b^2 kT}{Z^3 N e^4} \left(p_{E2a} + p_{E2b}\right),
\end{aligned}
\tag{3.3}
$$

with the p's given by (2.9, 23, 24, and 26). The value of $g_0(\zeta)$ is well known (See for example Huang [12]) and is given by

$$
g_0(\zeta) = \frac{2 I_{\frac{3}{2}}(z)}{3 I_{\frac{1}{2}}(z)}, \tag{3.4}
$$

where $z = \exp(\mu/kT)$ is the fugacity and ζ is given by

$$
\zeta = \frac{2}{\sqrt{\pi}} I_{\frac{1}{2}}(z), \tag{3.5}
$$

and

$$
I_n(z) = \int_0^\infty \frac{z y^n e^{-y}\, dy}{1 + z e^{-y}}. \tag{3.6}
$$

The expansions of both ζ and $g_0(z)$ in powers of the fugacity z are also well known and easily derivable from the straightforward expansions

$$
I_n(z) = \Gamma(n+1) \sum_{j=1}^{\infty} \frac{(-1)^{j+1} z^j}{j^{n+1}}, \quad n > -1. \tag{3.7}
$$

The goal of this section is to expand all the g_j's in series in the fugacity. In the next section we use the results of Baker and Johnson [3] who have reverted the series for $\zeta(z)$ to give the series for the fugacity in powers of the de Broglie density $z(\zeta)$. This method will permit the expression of all the g_j's as series expansions in powers of the de Broglie density. Baker and Johnson [3] give the first 36 terms of the expansion for $g_0(\zeta)$ and 37 terms for $z(\zeta)$. This computation required the retention of a great many decimal places because it is numerically very ill-conditioned.

The deduction of the series for $g_2(\zeta)$ may be reduced to previous work (Baker and Johnson [4]). If in (2.9) we make the change of variables, $y_i = \hbar^2 k_i^2/(2mkT)$ for $i = 1, 2$ and then integrate over the angles we get,

$$
\begin{aligned}
p_{E1} &= -\frac{4\pi e^2}{(2\pi)^6} 2\pi^2 \left(\frac{2mkT}{\hbar^2}\right)^2 \int_0^\infty \int_0^\infty \frac{\ln\left|\dfrac{\sqrt{y_1}+\sqrt{y_2}}{\sqrt{y_1}-\sqrt{y_2}}\right|}{(e^{-y_1} z^{-1} + 1)(e^{-y_2} z^{-1} + 1)}\, dy_1\, dy_2 \\
&= -\frac{4\pi e^2}{(2\pi)^6} 2\pi^2 \left(\frac{2mkT}{\hbar^2}\right)^2 X(\zeta) = -\frac{8\pi e^2 m^2 (kT)^2}{h^4} X(\zeta),
\end{aligned}
\tag{3.8}
$$

where $X(\zeta)$ agrees with that of (7.2) of Baker and Johnson [4]. They give the result,

$$X(\zeta) = \pi \sum_{n_1,n_2=1}^{\infty} \frac{(-z)^{n_1+n_2}}{\sqrt{n_1 n_2}(n_1+n_2)}. \tag{3.9}$$

In the Debye-Hückel pressure (2.23) we have the integral,

$$\begin{aligned}\int d\vec{k}\,\mathrm{sech}^2\left(\frac{\epsilon(\vec{k})-\mu}{2kT}\right) &= 8\pi\left(\frac{2mkT}{\hbar^2}\right)^{\frac{3}{2}}\int_0^\infty \frac{zy^{\frac{1}{2}}e^{-y}\,dy}{(1+ze^{-y})^2}\\ &= 8\pi\Gamma(\frac{3}{2})\left(\frac{2mkT}{\hbar^2}\right)^{\frac{3}{2}}\sum_{j=1}^{\infty}\frac{(-1)^{j+1}z^j}{j^{\frac{1}{2}}}\\ &= 4\pi\left(\frac{2mkT}{\hbar^2}\right)^{\frac{3}{2}} I_{-\frac{1}{2}}(z)\end{aligned} \tag{3.10}$$

In p_{E2a} (2.24) there appears the integral,

$$\begin{aligned}&\int \frac{d\vec{k}_1\,d\vec{k}_2\,d\vec{q}}{q^2(\vec{q}+\vec{k}_1-\vec{k}_2)^2}\frac{\sinh(\vec{q}\cdot(\vec{q}+\vec{k}_1-\vec{k}_2))}{\vec{q}\cdot(\vec{q}+\vec{k}_1-\vec{k}_2)}\left[\cosh\left(\frac{(\vec{q}+\vec{k}_1)^2}{2}-\frac{\mu}{2kT}\right)\right.\\ &\left.\times\cosh\left(\frac{k_1^2}{2}-\frac{\mu}{2kT}\right)\cosh\left(\frac{(\vec{k}_2-\vec{q})^2}{2}-\frac{\mu}{2kT}\right)\cosh\left(\frac{k_2^2}{2}-\frac{\mu}{2kT}\right)\right]^{-1},\end{aligned} \tag{3.11}$$

which using the notation $\eta = \log z = \mu/(kT)$ we can rewrite (3.11) as,

$$\begin{aligned}&2^3\int \frac{d\vec{k}_1\,d\vec{k}_2\,d\vec{q}}{q^2(\vec{q}+\vec{k}_1-\vec{k}_2)^2}\int_{-1}^{1} d\lambda\,\exp[\lambda\vec{q}\cdot(\vec{q}+\vec{k}_1-\vec{k}_2)]\\ &\qquad\times\frac{\exp[2\eta-q^2-\vec{q}\cdot(\vec{k}_1-\vec{k}_2)-k_1^2-k_2^2]}{(1+e^{\eta-(\vec{q}+\vec{k}_1)^2})(1+e^{\eta-k_1^2})(1+e^{\eta-(\vec{q}-\vec{k}_2)^2})(1+e^{\eta-k_2^2})},\end{aligned} \tag{3.12}$$

where we have artificially introduced the integral over λ for later convenience. Next let us make the change of variables, $\vec{k}_3 = \vec{k}_2 - \vec{k}_1 - \vec{q}$. We now expand the denominator in powers of z as we have done before, and we obtain,

$$\begin{aligned}&2^3\sum_{j_1,j_2,j_3,j_4=0}^{\infty}(-1)^{j_1+j_2+j_3+j_4}\int\frac{d\vec{q}\,d\vec{k}_1\,d\vec{k}_3}{q^2k_3^2}\int_{-1}^{1}d\lambda\,\exp[(2+j_1+j_2+j_3+j_4)\eta-2k_1^2\\ &-k_3^2-q^2-2\vec{q}\cdot\vec{k}_1-2\vec{k}_1\cdot\vec{k}_3-(1+\lambda)\vec{q}\cdot\vec{k}_3-j_1(\vec{q}+\vec{k}_1)^2-j_2k_1^2-j_3(\vec{k}_1+\vec{k}_3)^2-j_4(\vec{k}_1+\vec{k}_3+\vec{q})^2]\end{aligned} \tag{3.13}$$

If we now look at the integration over $\vec{k}_1$, we may do it by completing the square in the exponent, and integrating over the cartesian coordinates. The step yields,

$$\begin{aligned}&2^3\pi^{\frac{3}{2}}\sum_{j_1,j_2,j_3,j_4=0}^{\infty}\frac{(-1)^{j_1+j_2+j_3+j_4}}{(2+j_1+j_2+j_3+j_4)^{\frac{3}{2}}}\int\frac{d\vec{q}\,d\vec{k}_3}{q^2k_3^2}\int_{-1}^{1}d\lambda\,\exp\{(2+j_1+j_2+j_3+j_4)\eta\\ &-[(1+j_1+j_2)(1+j_3+j_4)k_3^2+((2+j_1+j_2+j_3+j_4)(1+2j_4)-2(1+j_1+j_4)(1+j_3+j_4)\\ &+\lambda(2+j_1+j_2+j_3+j_4))\vec{q}\cdot\vec{k}_3+(1+j_1+j_4)(1+j_2+j_3)q^2]/(2+j_1+j_2+j_3+j_4)\}.\end{aligned} \tag{3.14}$$

The next step is to do the integrals over all the angles except that between $\vec{q}$ and $\vec{k}_1$, whose cosine we denote as τ. Then, doing the integral over amplitudes by the standard method for a quadratic form in the exponent, we get,

$$2^4\pi^{\frac{9}{2}} \sum_{j_1,j_2,j_3,j_4=0}^{\infty} \frac{(-1)^{j_1+j_2+j_3+j_4}}{\sqrt{2+j_1+j_2+j_3+j_4}} \int_{-1}^{1} d\lambda \, \exp[(2+j_1+j_2+j_3+j_4)\eta] \times \int_{-1}^{1} \frac{d\tau}{\sqrt{AC-B^2\tau^2}}, \quad (3.15)$$

where

$$\begin{aligned} AC &= (1+j_1+j_2)(1+j_3+j_4)(1+j_1+j_4)(1+j_2+j_3) \\ B &= a+b\lambda \\ a &= (2+j_1+j_2+j_3+j_4)(\tfrac{1}{2}+j_4)-(1+j_1+j_4)(1+j_3+j_4) \\ b &= \tfrac{1}{2}(2+j_1+j_2+j_3+j_4) \end{aligned} \quad (3.16)$$

The integral over τ is elementary and yields,

$$2^5\pi^{\frac{9}{2}}T(\zeta) = 2^5\pi^{\frac{9}{2}} \sum_{j_1,j_2,j_3,j_4=0}^{\infty} \frac{(-1)^{j_1+j_2+j_3+j_4} z^{2+j_1+j_2+j_3+j_4}}{b\sqrt{2+j_1+j_2+j_3+j_4}} \int_{-1}^{1} \frac{b\,d\lambda}{a+b\lambda} \sin^{-1}\left(\frac{a+b\lambda}{\sqrt{AC}}\right), \quad (3.17)$$

which yields the expansion and defines $T(\zeta)$ for later use. As a practical matter, we still need to do the integral over λ. It can be evaluated in terms of dilogarithms of complex argument (Gröbner and Hofreiter [13], 341.4b) which does not improve the situation much over direct evaluation. The substitution which we will make in the next section in order to convert to a series in ζ is numerically ill-conditioned so we need a method which will yield highly accurate values. The integral we need to evaluate is of the form

$$\int_0^v \frac{d\nu}{\nu} \sin^{-1}(\nu) = \sum_{k=0}^{\infty} \frac{(\frac{1}{2})_k v^{2k+1}}{k!(2k+1)^2}, \quad (3.18)$$

where we use the notation,

$$(g)_0 = 1, \quad (g)_k = g\cdot(g+1)\cdots(g+k-1), \quad k \geq 1. \quad (3.19)$$

The radius of convergence of the series (3.18) is $|v| = 1$. Its use when $v \approx \pm 1$ is too slow to be practical. We know that the nature of those singularities is $\sqrt{1-v^2}$. A uniformizing transformation which regularizes $\sqrt{1-v^2}$ will make the whole function regular at $v = \pm 1$. We choose the transformation,

$$v^2 = \frac{8w^2(3-w^2)}{9+6w^2+w^4}, \quad (3.20)$$

which converts,

$$\sqrt{(1-v^2)} = \frac{1-w^2}{1+\frac{1}{3}w^2}. \quad (3.21)$$

and makes the points $v = \pm 1$ into regular points $w = \pm 1$. There will be singular points at $w = \pm i\sqrt{3}$ which leaves a radius of convergence of 3 in w^2. This improvement is adequate for our purposes. The substitution of (3.20) in the series (3.18) must be done with care as many decimal places will be lost in the tripling of the radius of convergence. Never-the-less, we have carried this computation out in multiple precision arithmetic (58 decimals) and obtained adequate accuracy to evalute the series coefficients in (3.17).

The contribution to the pressure p_{E2b} contains the integral,

$$\int \frac{d\vec{k}_1\, d\vec{k}_2\, d\vec{k}_3}{(\vec{k}_2 - \vec{k}_1)^2(\vec{k}_1 - \vec{k}_3)^2} \frac{\operatorname{sech}^2\left(\frac{1}{2}k_1^2 - \frac{\mu}{2kT}\right)}{\left[1 + \exp\left(k_2^2 - \frac{\mu}{kT}\right)\right]\left[1 + \exp\left(k_3^2 - \frac{\mu}{kT}\right)\right]}. \tag{3.22}$$

Let us make the change of variables $\vec{p}_1 = \vec{k}_2 - \vec{k}_1$ and $\vec{p}_2 = \vec{k}_3 - \vec{k}_1$. If we now expand (3.22) in powers of z, as we did above, we obtain,

$$4 \sum_{j_1,j_2,j_3=1}^{\infty} j_3(-1)^{j_1+j_2+j_3-3} e^{(j_1+j_2+j_3)\eta} \int \frac{d\vec{p}_1\, d\vec{p}_2}{p_1^2 p_2^2} d\vec{k}_1\, \exp(-j_1 p_1^2 - j_2 p_2^2 - (j_1 + j_2 + j_3)k_1^2 - 2j_1\vec{p}_1 \cdot \vec{k}_1 - 2j_2\vec{p}_2 \cdot \vec{k}_1). \tag{3.23}$$

If we integrate over $\vec{k}_1$ by completing the square in cartesian coordinates, then (3.23) becomes,

$$4\pi^{\frac{3}{2}} \sum_{j_1,j_2,j_3=1}^{\infty} \frac{j_3(-1)^{j_1+j_2+j_3-3} e^{(j_1+j_2+j_3)\eta}}{(j_1 + j_2 + j_3)^{\frac{3}{2}}} \int \frac{d\vec{p}_1\, d\vec{p}_2}{p_1^2 p_2^2} \times \exp\left(\frac{-j_1(j_2 + j_3)p_1^2 - j_2(j_1 + j_3)p_2^2 + 2j_1 j_2 \vec{p}_1 \cdot \vec{p}_2}{j_1 + j_2 + j_3}\right). \tag{3.24}$$

If we integrate over all the angles except that between $\vec{p}_1$ and $\vec{p}_2$ and denote the cosine of that angle by τ, then if we integrate over the magnitudes in the standard way for a quadratic form in the exponent, we get

$$8\pi^3 \pi^{\frac{3}{2}} \sum_{j_1,j_2,j_3=1}^{\infty} \frac{j_3(-1)^{j_1+j_2+j_3-3} e^{(j_1+j_2+j_3)\eta}}{j_1 j_2 (j_1 + j_2 + j_3)^{\frac{1}{2}}} \times \int_{-1}^{1} \frac{\sqrt{j_1 j_2}\, d\tau}{(j_3(j_2 + j_1) + j_3^2 + j_1 j_2(1 - \tau^2))^{\frac{1}{2}}}. \tag{3.25}$$

The final integral can now be evaluated to yield,

$$16\pi^{\frac{9}{2}} \sum_{j_1,j_2,j_3=1}^{\infty} \frac{j_3(-1)^{j_1+j_2+j_3-3} e^{(j_1+j_2+j_3)\eta}}{j_1 j_2 (j_1 + j_2 + j_3)^{\frac{1}{2}}} \sin^{-1}\left(\sqrt{\frac{j_1 j_2}{(j_1 + j_3)(j_2 + j_3)}}\right), \tag{3.26}$$

which can be rearranged in the slightly more convenient form,

$$16\pi^{\frac{9}{2}} \Theta(\zeta) = 16\pi^{\frac{9}{2}} \sum_{J=3}^{\infty} \frac{-(-z)^J}{\sqrt{J}} \sum_{j_1=1}^{J-2} \sum_{j_2=1}^{J-j_1-1} \frac{J - j_1 - j_2}{j_1 j_2} \sin^{-1}\left(\sqrt{\frac{j_1 j_2}{(J - j_1)(J - j_2)}}\right), \tag{3.27}$$

which also defines $\Theta(\zeta)$ for later use.

This calculation completes all the necessary ingredients to expand the various contributions to the pressure in powers of the fugacity.

It is useful at this point to recapitulate the resulting values of the $g_i(\zeta)$ of (3.3). They are

$$\begin{aligned} g_2(\zeta) &= -\frac{1}{2\pi Z^{2/3}}\left(\frac{3}{\pi}\right)^{\frac{1}{3}}\zeta^{-\frac{4}{3}}X(\zeta) \\ g_3(\zeta) &= -\frac{1}{Z\sqrt{3}}\left[\hat{Z}+\frac{1}{g_0(\zeta)+\zeta g_0'(\zeta)}\right]^{\frac{3}{2}} \\ g_4(\zeta) &= \frac{1}{8Z^{4/3}}\left(\frac{3}{\pi}\right)^{\frac{2}{3}}\zeta^{-\frac{5}{3}}[T(\zeta)+2\Theta(\zeta)], \end{aligned} \tag{3.28}$$

where $g_0(\zeta)$ is given by (3.4), $X(\zeta)$ by (3.9), $T(\zeta)$ by (3.17) and $\Theta(\zeta)$ by (3.27). For a pure element, $\hat{Z}=Z$. In the case of mixtures we can compute,

$$Z=\frac{\sum_{\text{species}} N_j Z_j}{\sum_{\text{species}} N_j}, \quad \hat{Z}=\frac{\sum_{\text{species}} N_j Z_j^2}{\sum_{\text{species}} N_j Z_j}, \tag{3.29}$$

where N_j is the number of ions and Z_j is the nuclear charge in each species.

IV. REPRESENTATION OF THE COEFFICIENTS AS FUNCTIONS OF THE DE BROGLIE DENSITY.

In the previous section we have derived series expansions in the fugacity z for the various functions need to calculate the expansion of the pressure in powers of the electronic charge. While is is possible to express the fugacity in terms of the de Broglie density (3.2) by the inversion of (3.5) and to give a compact representation there of, it is more convenient to work directly in terms of the de Broglie density. It is our aim in this section to produce representations of the various quantities as functions of the de Broglie density which are accurate to within about 0.1%. The series for the fugacity in powers of the de Broglie density (for the idea Fermi gas which is what we actually require) has been given by Baker and Johnson [5]. It can be substituted into the expressions of the previous section to give the required series in the de Broglie density. Then following the method of Padé approximants [14], we can construct the require representations. Although it is not required in this work, we give, for the convenience of the reader, the following representation for the fugacity $z(\zeta)$ as,

$$z(\zeta)\approx\exp\{\zeta[\hat{\theta}(\zeta)]^{\frac{1}{3}}\}-1, \tag{4.1}$$

where,

$$\hat{\theta}(\zeta)=\frac{1+0.23728611\zeta+2.4737617\times10^{-2}\zeta^2+1.4222435\times10^{-3}\zeta^3}{1+0.67662597\zeta+0.14567696\zeta^2+1.4254337\times10^{-2}\zeta^3+8.0482522\times10^{-4}\zeta^4} \tag{4.2}$$

within 0.1%.

For the convenience of the reader, we recapitulate the previous results of Baker and Johnson [3] for $g_0(\zeta)$

$$g_0(\zeta)\approx\left[\frac{1+0.61094880\zeta+0.12660436\zeta^2+0.0091177644\zeta^3}{1+0.080618739\zeta}\right]^{\frac{1}{3}}, \tag{4.3}$$

The general method we use to obtain these representations is first to compute a fair number of terms in the series expansion. Even with an explicit representation for the series as a function of the fugacity, care must be taken in the re-expression as a function of the de Broglie density because the problem is numerically ill-conditioned, and many decimal places can be lost. We have found that the retention of 58 decimals is sufficient for all our purposes. The next step is to determine the asymptotic behavior. From this information, we compute a function of the original series (*e.g.*, the cube) which can be exactly represented, both at the origin and at infinity, by a Padé approximant. We then compute a sequence of Padé approximants and use the lowest order one which gives the desired degree of accuracy. Since, for our problems, these sequences converge fairly quickly, this method seems to be quite efficient.

Using these methods, we obtain for $X(\zeta)$,

$$X(\zeta) \approx \zeta^2 \frac{\pi}{2} \left[\frac{1 + 0.088412769\zeta}{1 + 0.79551953\zeta + 0.19350034\zeta^2 + 0.013716390\zeta^3} \right]^{\frac{1}{3}}, \tag{4.4}$$

where

$$X(\zeta) \asymp 2 \left[\frac{3\sqrt{\pi}}{4} \zeta \right]^{\frac{4}{3}} \quad \text{as} \quad \zeta \to \infty. \tag{4.5}$$

Since differentiation does not necessarily preserve the accuracy of approximation, instead of using (4.2), use the separate representation of Baker and Johnson [4],

$$\frac{1}{g_0(\zeta) + \zeta g_0'(\zeta)} \approx \left[\frac{v_3(\zeta)}{u_5(\zeta)} \right]^{\frac{1}{3}}, \tag{4.6}$$

where

$$\begin{aligned} v_3(\zeta) =& 1 + 0.17549205\zeta + 1.1833437 \times 10^{-2}\zeta^2 + 3.0923597 \times 10^{-4}\zeta^3, \\ u_5(\zeta) =& 1 + 1.2361522\zeta + 0.54327035\zeta^2 + 9.7985998 \times 10^{-2}\zeta^3 \\ & + 6.1912639 \times 10^{-3}\zeta^4 + 1.6191557 \times 10^{-4}\zeta^5. \end{aligned} \tag{4.7}$$

For $\Theta(\zeta)$, using the result,

$$\Theta(\zeta) \asymp \frac{3}{2\pi}\zeta \quad \text{as} \quad \zeta \to \infty, \tag{4.8}$$

which is obtained by taking the limit as $z \to \infty$ of Θ and ζ and evaluating their integral definitions, we obtain the representation

$$\Theta(\zeta) \approx \frac{\mu_6(\zeta)}{\theta_5(\zeta)}, \tag{4.9}$$

where

$$\begin{aligned} \mu_6(\zeta) =& 0.30229989\zeta^3 + 5.0287616 \times 10^{-2}\zeta^4 + 3.6103004 \times 10^{-3}\zeta^5 \\ & + 1.0210313 \times 10^{-4}\zeta^6, \\ \theta_5(\zeta) =& 1 + 1.2478566\zeta + 0.55778521\zeta^2 + 0.10432105\zeta^3 \\ & + 7.2823921 \times 10^{-3}\zeta^4 + 2.1384429 \times 10^{-4}\zeta^5. \end{aligned} \tag{4.10}$$

The representation of $T(\zeta)$ presents an additional problem not present for the other functions. The asymptotic value as $\zeta \to \infty$ is proportional to ζ, as in the case of Θ, but here we have not been able to evaluate the asymptotic coefficient analytically. This coefficient is the zero temperature diagram evaluated approximately by Monte Carlo by Gell-Mann and Brueckner [7] in their study of the electon-gas correlation energy. We have taken a different approach to its evaluation. We have computed the series through the 31st order and obtain the asymptotic result,

$$\frac{T(\zeta)}{\zeta} \asymp 0.3025 \pm 0.0004, \tag{4.11}$$

where it is the apparent error which we have quoted. This result corresponds to $\epsilon_b^{(2)} = 0.04814 \pm 0.00006$ in the notation of Gell-Mann and Brueckner, in agreement with their result of 0.046 ± 0.002. When we use this asymptotic value, we obtain the representation,

$$T(\zeta) \approx \frac{\nu_6(\zeta)}{\tau_5(\zeta)}, \tag{4.12}$$

where

$$\begin{aligned}\nu_6(\zeta) =& 1.5397859\zeta^2 + 0.681831\zeta^3 + 0.10939850\zeta^4 \\ &+ 8.8741342 \times 10^{-3}\zeta^5 + 2.67165364 \times 10^{-4}\zeta^6 \\ \tau_5(\zeta) =& 1 + 1.3317659\zeta + 0.66394907\zeta^2 + 0.15311424\zeta^3 \\ &+ 1.6850905 \times 10^{-2}\zeta^4 + 8.8319130 \times 10^{-4}\zeta^5.\end{aligned} \tag{4.13}$$

These results supply the necessary representations to compute the $g_i(\zeta)$ of the previous section to within 0.1%.

V. GLOBAL PRESSURE REPRESENTATION.

In a previous paper [5], we derived a global representation of the Thomas Fermi pressure. We used as input the corresponding expansion in e for Thomas-Fermi pressure, and information on the asymptotic behavour at low density for fixed de Broglie density. We have subsequently found that there was an error of a factor of 2 in (4.9) of reference 4, which meant there was an error of a factor of two in the corresponding Thomas-Fermi g_4. We have corrected this error, removed an extraneous factor of $Z^{\frac{4}{3}}$ in (4.8) of reference 5, and thus the appropriate representation for ΔP where,

$$P = \Delta P + P_{\text{cold curve}}, \tag{5.1}$$

with $P_{\text{cold curve}}$ the zero temperature pressure as a function of density, is

$$\Delta P \approx \frac{196.6889 Z^{\frac{10}{3}} x^{-5} \tilde{g}_0(\zeta)}{\left[1 - 2\dfrac{\tilde{g}_4(\zeta)x^2}{\tilde{g}_0(\zeta)(1+0.008x)} + \left\{\dfrac{\zeta^{\frac{7}{6}}\tilde{g}_0(\zeta)}{d_0}\right\}^2 x^3\right]^{\frac{1}{2}}}. \tag{5.2}$$

We use the notation,

$$x = \left(\frac{128Z}{9\pi^2}\right)^{\frac{1}{3}} \frac{me^2 r_b}{\hbar^2}, \quad y = \left(\frac{\sqrt{\pi}}{4}\zeta\right)^{\frac{1}{3}} \sqrt{x}, \tag{5.3}$$

$$\hat{g}_j = \lim_{\zeta\to\infty} g_j(\zeta)\zeta^{(j-2)/3}, \tag{5.4}$$

$$\tilde{g}_j(\zeta) = \left(\frac{\sqrt{\pi}}{4}\right)^{j/3} [g_j(\zeta)\zeta^{(j-2)/3} - \hat{g}_j]. \tag{5.5}$$

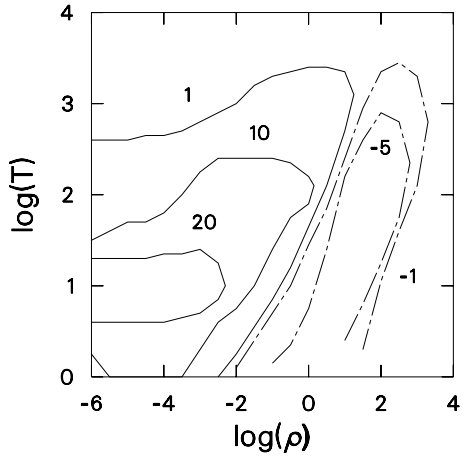

Fig. 6. Contour lines in percent for the difference between our quantum theory pressure and Thomas-Fermi theory pressure for Aluminum. The temperature is in electron volts and the density is measured in units of the normal density.

Through the use of (5.3), (3.1) is readily converted into an expansion in $\sqrt{x}$ and (5.2) was constructed to match that expansion through order $(\sqrt{x}\,)^4$ for Thomas-Fermi theory. The behavior of the $\tilde{g}_4$ term has been modified at large x in order that the x^2, $x^{2.5}$, x^3 terms for large x should all have their origin in the last term of the denominator of (5.3). The value 0.008 was selected to prevent an underpressure due to the $\tilde{g}_4$ term at large x. We have a revised fit for d_0 of the same form as in reference 5 and it is

$$d_0 = \frac{34.201282 + (257.72103\zeta^{\frac{1}{6}} - 161.51875)\zeta^{\frac{1}{6}}/\sqrt{x}}{1 + 14.591736\zeta^{\frac{1}{6}}/\sqrt{x}}. \tag{5.5}$$

The representation which we now employ is

$$\Delta P \approx \tag{5.6}$$

$$\frac{196.6889 Z^{\frac{10}{3}} x^{-5} \tilde{g}_0(\zeta)}{\left[1 - 2x\frac{\tilde{g}_2(\zeta)}{\tilde{g}_0(\zeta)} - \frac{2x^{\frac{3}{2}}\frac{\tilde{g}_3(\zeta)}{\tilde{g}_0(\zeta)} + x^2\left(2\frac{\tilde{g}_4(\zeta)}{\tilde{g}_0(\zeta)} - 3\left(\frac{\tilde{g}_2(\zeta)}{\tilde{g}_0(\zeta)}\right)^2\right)}{1 + 0.008x} + x^3\left\{\frac{\zeta^{\frac{7}{6}}\tilde{g}_0(\zeta)}{d_0}\right\}^2\right]^{\frac{1}{2}}},$$

which matches the small $x^{\frac{1}{2}}$-expansion through order $(x^{\frac{1}{2}})^4$ as determined in the previous sections, and matches the large x behavior, as described above, of the Thomas-Fermi theory. Note is taken that there remains the problem of determing the proper quantum mechanical results for very dilute systems.

In Fig. 6 we have displayed graphically the difference for the pressure between our many-body theory and the Thomas-Fermi theory for the case of Aluminum. The Thomas-Fermi cold-curve is used in both cases. Since it is rather poor, a more realistic curve should be used for practical work. In Fig. 7, we display the differences for Cesium. It will be seen that there is little difference at the highest temperatures and that, generally speaking, we obtain lower pressures at higher densities and higher pressures at lower densities. The order of magnitude of the effect is double digit percentages.

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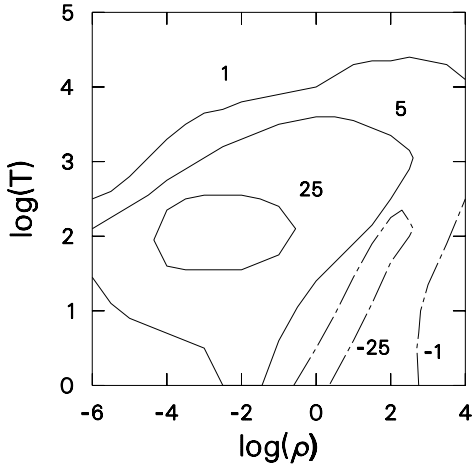

Fig. 7. Contour lines in percent for the difference between our quantum theory pressure and Thomas-Fermi theory pressure for Cesium. The temperature is in electron volts and the density is measured in units of the normal density.

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