

## Effective potentials and Yuri Lvovich Klimontovich

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# Effective Potentials and Yuri Lvovich Klimontovich

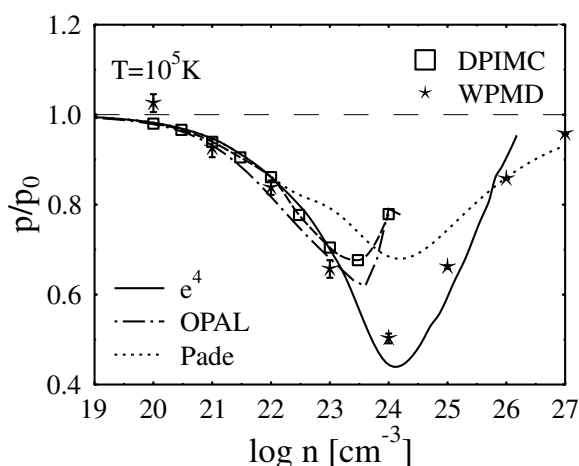
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**Abstract.** The application of effective potentials is discussed. Special problems and discrepancies are addressed.

## 1. Introduction

For the determination of properties of many-particle quantum systems, there exist general theoretical schemes both for equilibrium and transport properties. Analytic results are known for limiting cases only, namely for weakly and strongly degenerate systems. In the intermediate region, numerical simulations or interpolations by Padé formulae have to be applied. An urgent demand is to achieve agreement between analytical calculations and numerical experiments in limiting situations. This is not the case yet, as one can see, e.g., in Fig. 1. Discrepancies in the



**Figure 1.** Hydrogen pressure from different theoretical procedures:  $e^4$  and Padé-[1], WPMD- [2], OPAL- [3], DPIM-[4]

EOS data lead to a wide spread of the theoretically determined Hugoniot curves which do not agree with experimental results, see [5]-[7].

There are several techniques to overcome different types of difficulties. One of such possibilities is the application of *effective* quantities, such as effective potentials, effective fields, effective ionization energies, etc.

The book of [8] mentions the term *effective* several times. In [9], the term *effective* is used 177 times. The goal is mostly to systematize or to simplify calculations, e.g., by application of

techniques usually applicable (only) to classical systems. However, there is no general scheme, how to find effective potentials. The special choice is determined by practical purposes.

There are several exactly justified ways: (i) *Partial summation* is applied to avoid long range divergencies. The result is, e.g., the Debye potential. With the application of this potential, long range divergencies are avoided *classically*. In thermodynamics, e.g., we get the limiting law  $n^{3/2}$  and the logarithmic term  $n^2 \log n$ . (ii) Short range divergencies for point charges can be avoided only by methods of *quantum mechanics*; evaluation of the Slater–sum leads to effective (*Kelbg*) potentials (see below) with finite  $r = 0$  values. Reasonable (exact) results for the thermodynamics in the low degeneracy quantum limit are then achieved using classical schemes [10]. Further consequent schemes are (iii) the theory of pseudo–potentials for ions accounting for the shell structure, and (iv) close coupling calculations for deviations from point or spherically symmetric structures.

More or less *pragmatic* possibilities are the (a) fit to experimental data or the fit to bound state energies, furthermore (b) hard core models, (c) confined atom and *particle in cell* schemes. Simplifications may also be achieved by (d) averaging procedures.

We give an example, in which the square of the dielectric function as used in the collision integral of the Lenard–Balescu kinetic equation is given in *three different* approximations. The first one is due to [8] and [11] using a special  $\omega$ –averaging

$$\left\langle \frac{1}{|\epsilon(\omega, \vec{k})|^2} \right\rangle |_{\omega-av} = \frac{k^2 r_D^2}{1 + k^2 r_D^2} = \frac{1}{1 + \kappa^2/k^2}, \quad \kappa = 1/r_D. \quad (1)$$

A very crude approximation is to take the limit  $\omega = 0$  instead of averaging

$$\left\langle \frac{1}{|\epsilon(\omega, \vec{k})|^2} \right\rangle \sim \frac{1}{(1 + \kappa^2/k^2)^2} \sim \frac{1}{1 + 2\kappa^2/k^2}. \quad (2)$$

In [12], a more detailed  $\omega$ –averaging is performed to give the result

$$\left\langle \frac{1}{|\epsilon(\omega, \vec{k})|^2} \right\rangle |_{\omega-av} = \frac{1}{\epsilon_e(0, \vec{k})} \frac{1}{\epsilon(0, \vec{k})} = \frac{1}{1 + \kappa^2/2k^2} \frac{1}{1 + \kappa^2/k^2} \sim \frac{1}{1 + 3\kappa^2/2k^2}. \quad (3)$$

For small  $\kappa$ , (2),(3) correspond to static Debye screening with a modified screening parameter, namely  $\sqrt{2}\kappa$  and  $\sqrt{3/2}\kappa$  instead of  $\kappa$  like in (1).

Another example is the effective potential as given in [8] for the equilibrium case

$$\tilde{v}_{ab}(k) = \frac{e_a e_b}{\sum_c e_c^2 n_c} \frac{(\delta \vec{E} \delta \vec{E})|_{k,t}}{4\pi} = 4\pi e_a e_b \frac{r_D^2}{1 + r_D^2 k^2} = \frac{4\pi e_a e_b}{\kappa^2 + k^2}, \quad (4)$$

where the equilibrium relation

$$(\delta \vec{E} \delta \vec{E})|_{k,t} = \frac{4\pi k_B T}{1 + r_D^2 k^2}$$

was used.

## 2. Application of effective potentials

The justification of effective potentials has to be considered. If one wants to apply HNC techniques, one must not use a screened potential as an input as the technique itself establishes screening. However, one may use a quantum potential in classical schemes for the determination

of the binary distribution function in order to include some quantum effects.

For the determination of the mean value of the potential energy (for point charges at least) one should in any case use the bare Coulomb potential and account for many body and/or quantum effects *only* in the determination of the distribution functions. We give two examples which lead to wrong results if, instead of the bare Coulomb potential, the Debye or the Kelbg potentials [13] are applied

$$\begin{aligned}\langle V \rangle &= \frac{1}{2} \int d\mathbf{r} V^{\text{coul}}(r) g^{\text{class}}(r) \sim \frac{\kappa^3}{k_B T}, \\ &\neq \frac{1}{2} \int d\mathbf{r} V^{\text{Deb}}(r) g^{\text{class}}(r) \sim \frac{1}{2} \frac{\kappa^3}{k_B T}.\end{aligned}\quad (5)$$

$$\begin{aligned}\langle V \rangle &= \frac{1}{2} \int d\mathbf{r} V^{\text{coul}}(r) g^{\text{qu}}(r) = 0 + \mathcal{O}((e^2)^{3/2}) + \text{exch} + \dots, \\ &\neq \frac{1}{2} \int d\mathbf{r} V^{\text{Kelbg}}(r) g^{\text{qu}}(r) = c \cdot e^2 + \mathcal{O}((e^2)^{3/2}) + \text{exch} + \dots.\end{aligned}\quad (6)$$

### 3. Slater sum and effective potential

Quantum effects produce short range corrections to the (binary) distribution function which may be expressed in terms of an additional short range correction  $V'_{ab}(\mathbf{r})$  to the Coulomb potential  $V_{ab}(\mathbf{r})$  and may be written using the (two-particle) *Slater sum*  $S_{ab}(\mathbf{r})$ . With

$$g_{ab}(\mathbf{r}) = -\frac{e_a e_b}{k_B T \mathbf{r}} \exp(-\kappa \mathbf{r}),$$

the distribution function was determined to be [14]-[18]

$$\begin{aligned}F_{ab}(\mathbf{r}_1 \mathbf{r}_2) &= \exp(g_{ab} - \beta V'_{ab}) \{1 + \dots\} = \exp(g_{ab} + \beta V_{ab}) S_{ab}(\mathbf{r}_1 \mathbf{r}_2) \{1 + \dots\}, \\ S_{ab}(r) &= \exp[-\beta(V_{ab}(r) + V'_{ab}(r))] = \exp(-\beta V_{ab}^{\text{eff}}(r)).\end{aligned}\quad (7)$$

We mention here that the terms indicated by dots in the curly brackets produce, in thermodynamic functions, terms of the same density orders as the unity does. There is a lowering of the orders in the density, so that terms having additional pre-factors  $n$  or even  $n^2$  lead to results of one or two lower density powers. In particular, the terms in question contribute to the  $n^2 e^6$  terms in thermodynamic functions (see the references just given). This means one has to be very careful in discussing higher powers of density.

Now we follow the idea outlined in [10]. If  $F_{ab}$  is known one may determine the mean value of the correlation energy  $E_{\text{corr}}$  for weakly degenerate quantum systems (including exchange contributions)

$$E_{\text{corr}} = \frac{1}{2} \sum_{ab} n_a N_b \int V_{ab} F_{ab} d\mathbf{r}.\quad (8)$$

Thermodynamic functions such as the free energy may then be determined by a charging procedure. The Slater sum contained in (7) was determined to give the following result for the effective potential [13]-[18]

$$V_{ab}^{\text{Kelbg}}(r) = \frac{e_a e_b}{r} \left[ 1 - \exp\left(-\frac{r^2}{\lambda_{ab}^2}\right) + \sqrt{\pi} \left(\frac{r}{\lambda_{ab}}\right) \left(1 - \Phi\left(\frac{r}{\lambda_{ab}}\right)\right) \right] + \mathcal{O}(e^4).\quad (9)$$

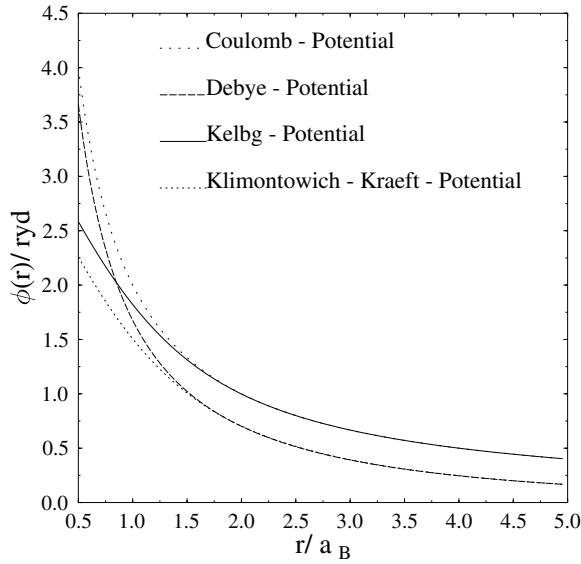
The exchange contribution to the effective potential reads

$$V_{ab}^{\text{exch}}(r) = \frac{\delta_{ab}}{2s_a + 1} \exp(-r^2/\lambda_{ab}^2) \left[ k_B T - \frac{e_a e_b}{r} \int_0^1 \frac{d\alpha}{\alpha} \Phi \left( \frac{r\alpha}{\lambda_{ab}\sqrt{(1-\alpha)}} \right) \right] + \mathcal{O}(e^4). \quad (10)$$

The direct potential (9) was determined in [13]. The screened version of the direct potential (9) reads [19, 20] with  $r_D$  being the Debye radius

$$V_{ab}^{\text{Kelbg,sc}}(r) = \frac{e_a e_b \pi^{1/2} r_D}{2\lambda_{ab}} \frac{1}{r} \left[ \exp \left( -\frac{r}{r_D} + \frac{\lambda_{ab}^2}{4r_D^2} \right) \times \left\{ \Phi \left( \frac{r}{\lambda_{ab}} - \frac{\lambda_{ab}}{2r_D} \right) + 2\Phi \left( \frac{\lambda_{ab}}{2r_D} \right) - 1 \right\} + \exp \left( \frac{r}{r_D} + \frac{\lambda_{ab}^2}{4r_D^2} \right) \left\{ 1 - \Phi \left( \frac{r}{\lambda_{ab}} + \frac{\lambda_{ab}}{2r_D} \right) \right\} \right]. \quad (11)$$

The Fig. 2 shows the Coulomb potential, the Debye potential, the (direct) Kelbg-potential (9)



**Figure 2.** Coulomb, Debye, Kelbg and screened Kelbg (Klimontovich–Kraeft) potentials

and its screened version (11). The latter two potentials are finite for  $r = 0$ . For long distances, (9) coincides with the Coulomb potential, and (11) behaves like the Debye potential.

Higher orders for effective potentials follow from the Slater sum excluding bound states [19]:

$$\tilde{u}_{ei}(r) = -e^2 \left( \frac{d}{a_0 + cr} + \frac{fr}{a_0^2 + r^2} \right) - \frac{e^2}{r} \left( e^{-r/r_D} - 1 \right), \quad (12)$$

where we have

$$\begin{aligned} d &= \frac{a_0}{e^2} k_B T \left( \frac{\xi_{ei}^2}{16} + \log \frac{\sqrt{\pi}}{8} \xi_{ei}^3 \right), \\ dc - f &= \frac{a_0}{e^2} k_B T \frac{a_0}{\lambda_{ei}} \xi_{ei}, \\ d/c + f &= 1, \end{aligned} \quad (13)$$

and  $\xi_{ei} = -e_e e_i / (k_B T \lambda_{ei})$ ,  $\lambda_{ei} = \hbar / (2\mu_{ei} k_B T)^{1/2}$ ,  $\mu_{ei}$  – reduced mass. At  $r = 0$ , we have

$$\tilde{u}_{ei}(r = 0) = -k_B T \left[ \frac{\xi_{ei}^2}{16} + \log \frac{\sqrt{\pi}}{8} \xi_{ei}^3 - \frac{\xi_{ei} \lambda_{ei}}{r_D} \right],$$

and for  $r \ll a_0$ ,

$$\tilde{u}_{ei}(r) = -\frac{e^2}{r} \exp -r/r_D.$$

Without screening, the expression (12) has to be improved to meet the exact long distance behavior  $1/r^4$  [21].

#### 4. Is there a $\xi/6$ - term in thermodynamics?

We repeat the calculation similar to that leading to the relation (5.62) in [22]. If one determines the Hartree contribution leading to (5.62) using the *Kelbg-potential* (9) instead of the Coulomb one, one *could* expand the (Fourier transform of the) Kelbg potential with respect to  $k$  using

$$V_{ab}(\mathbf{k}) {}_1F_1 \left( 1, \frac{3}{2}; -\frac{\lambda_{ab}^2 k^2}{4} \right) = \frac{e_a e_b}{\mathbf{k}^2} \left( 1 - \frac{2}{3} \frac{\lambda_{ab}^2 k^2}{4} + \dots \right).$$

This means, we have a nonzero contribution to the potential for  $\mathbf{k} = 0$ . In the general case, the Hartree pressure reads

$$p_H = -\frac{1}{2} \lim_{\mathbf{k} \rightarrow 0} \sum_{ab} (2s_a + 1)(2s_b + 1) V_{ab}(\mathbf{k}) \int \frac{d\mathbf{k}' d\mathbf{k}''}{(2\pi)^6} f_a(\mathbf{k}') f_b(\mathbf{k}'').$$

After integration, we get

$$p_H = -\frac{1}{2} \lim_{\mathbf{k} \rightarrow 0} \sum_{ab} \frac{4\pi e_a e_b n_a n_b}{\mathbf{k}^2} {}_1F_1 \left( 1, \frac{3}{2}; -\frac{\lambda_{ab}^2 k^2}{4} \right),$$

and more in detail

$$\int \delta(\mathbf{k}) V_{ab}(\mathbf{k}) d\mathbf{k} = \int \delta(\mathbf{k}) \left( \frac{4\pi e_a e_b}{k^2} + c \right) d\mathbf{k} = \frac{4\pi e_a e_b}{0} + C.$$

The divergent terms cancel each other on summation over species. The constant  $C$  corresponds to the additional term  $\xi_{ab}/6$ . We get

$$p_H = -\frac{1}{2} 4\pi n^2 e^2 \frac{1}{6} \frac{\hbar^2}{k_B T} \left[ \frac{1}{2m_{ee}} + \frac{1}{2m_{pp}} - \frac{2}{2m_{ep}} \right] = 0. \quad (14)$$

The single contributions of (14) correspond to the expressions in question  $\xi/6$  in the  $Q$ -function given below (18), [22].

In the papers by [23] and [24], there occurs a contribution linear in  $\xi$ . In the latter paper, this term is produced in the following way.

The Hartree term, which is divergent, is represented by the first r.h.s. term  $1/k^2$  of eq.(D60) in [24]. Here, in principle, the limiting value for  $k \rightarrow 0$  should be taken; however, instead an expansion is performed with respect to  $k$  leading to a non-divergent term of the order  $k^0$ , which is represented by the third r.h.s. term of eq.(D60),  $mz/(6\gamma^2)$ , which leads to the term  $1/(2\pi y^2)$  in eq.(D67) and corresponds exactly to the term  $\xi/6$  on the "level" of the  $Q$ -function (18).

The term is achieved by an expansion of expression (D40) with respect to small  $k$ :

$$\begin{aligned} G(\vec{k}, E) &= \frac{a_1}{k} \frac{1}{1 + (k/a_2)^2} \left[ \dots - \sin(a_3 k + a_4 k^3 + \dots)(a_5/k^2 + a_6 + \dots) \right] \\ &= \frac{b_1}{k^2} + \frac{b_2}{k} + b_3 k^0 + \dots \end{aligned} \quad (15)$$

Here, the term  $b_3 k^0$  corresponds to the term in question,  $\xi/6$ . The coefficients  $a_i$  and  $b_j$  do not depend on  $k$ . Even if there is no contribution except the one which is divergent for  $k = 0$ , the expression in square brackets of (14) is equal to zero and does not change the situation of vanishing contributions. However, if there is some multiplication of such terms prior to summation, there might be a contribution due to the fact that on one side

$$\sum_{ab} e_a e_b = 0,$$

however on the other hand

$$\sum_{ab} e_a^2 e_b^2 = \text{nonzero}.$$

Such situation occurs in equation (5.20) of [24]:

$$\sum_{ab} e_a e_b \Gamma_{ab} = 0 \quad \text{vs.} \quad \sum_{ab} e_a^2 e_b^2 \Gamma_{ab} = \text{nonzero}.$$

At least in a two component system with equal masses and opposite charges, one simply should omit the Hartree contributions as they cancel each other on behalf of electro-neutrality. Then, there is no argument for a  $k$ -expansion.

The direct term  $1/(\eta^2)$  in the Brown paper eq.(5.27) arises from the multiplication of the  $\eta^{-3}$  contribution of  $\Gamma$  with the factor  $g^3$  in the second line of (5.25). Without the  $\eta^{-3}$  term, the corresponding direct  $n^{5/2}$  term would *not arise at all*. Here the question is whether the appearance of  $n^{5/2}$  terms is substantially connected with the existence of the  $\xi/6$  term. In the thesis by [25] and in the papers [26]-[28], the  $n^{5/2}$  direct term comes from the quantum improved screening ( ${}_1F_1$ -functions, see next section). While the function  $G(\mathbf{k}E)$  for the direct term eq.(D39) of the paper by [24] is divergent for  $k = 0$ , but should be evaluated at  $k = 0$ , the situation is different for the exchange function  $G_-(\mathbf{k}E)$ , eq.(D78), which is finite for  $k = 0$ .

In the paper by [23], the existence of a  $\xi/6$ -term in (18) is assumed, and in this way terms of the order  $(ne^2)^{5/2}$  are produced.

## 5. EOS up to $n^2$ , $(ne^2)^{5/2}$

In the weakly degenerate case, we have the following result for the (fugacity) expansion of the pressure [22],[26]

$$\begin{aligned} \beta p = & \sum_a z_a + \frac{\kappa^3}{12\pi} + \sum_{ab} z_a z_b \lambda_{ab}^3 \left[ K_0(\xi_{ab}) - \frac{\xi_{ab}^3}{6} \ln \kappa \lambda_{ab} \right] \\ & + \frac{\kappa^3}{12\pi} \sum_a \left[ \frac{1}{8} \kappa_a^2 \lambda_{aa}^2 + \frac{3}{2(2s_a + 1)} \left( \kappa_a^2 \lambda_{aa}^2 - \frac{z_a \Lambda_a^3}{\sqrt{2}} \right) \frac{\kappa_a^2}{\kappa^2} \right]. \end{aligned} \quad (16)$$

Here we used modified fugacities  $z_c$  (tending to densities in the low density case) and

$$\kappa^2 = \sum_c \frac{4\pi z_c e_c^2}{k_B T}, \quad \kappa_a^2 = \frac{4\pi z_a e_a^2}{k_B T},$$

$$K_0(\xi) = Q(\xi) + \delta_{ab} \frac{(-1)^{2\sigma_a}}{2\sigma_a + 1} E(\xi) \quad (17)$$

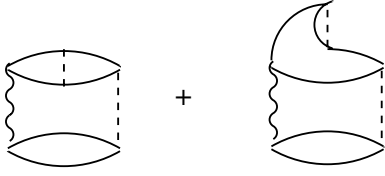
and

$$Q(\xi) = -\frac{\sqrt{\pi}}{8} \xi^2 - \frac{\xi^3}{6} \left( \frac{C}{2} + \ln 3 - \frac{1}{2} \right) + \sum_{p=4} \frac{\sqrt{\pi} \zeta(p-2)}{\Gamma(\frac{p}{2} + 1)} \left( \frac{\xi}{2} \right)^p. \quad (18)$$

We want to stress here once more that, according to our considerations in preceding sections, there is no term  $\xi/6$  in the direct contribution (18). The sum of exchange terms reads

$$E(\xi) = \frac{\sqrt{\pi}}{4} + \frac{\xi}{2} + \sqrt{\pi} \ln 2 \left(\frac{\xi}{2}\right)^2 + \frac{\pi^2}{9} \left(\frac{\xi}{2}\right)^3 + \sum_{p=4} \frac{\sqrt{\pi}(1-2^{2-p})\zeta(p-1)}{\Gamma(\frac{p}{2}+1)} \left(\frac{\xi}{2}\right)^p. \quad (19)$$

The results presented in the first line of (16) are well known and found in [22]. The contributions

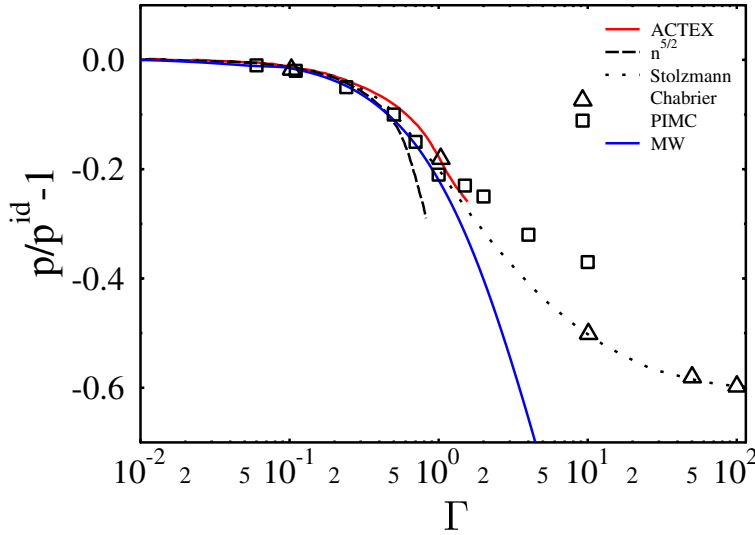


**Figure 3.** Vertex and self energy contributions beyond the Montroll Ward term (quantum ring sum) leading to  $n^{5/2}$  terms

of the second line include direct terms of the order  $(ne^2)^{5/2}$  which are produced by an improved screening as given by [25]-[28]

$$V_{aa}^{st}(\mathbf{k}, 0) = V_{aa}^s(\mathbf{k}, 0) = \frac{V_{aa}(\mathbf{k})}{1 + \sum_c (\kappa_c^2/k^2) {}_1F_1(1, 3/2; -\lambda_{cc}^2 k^2/8)}. \quad (20)$$

Furthermore, there are exchange contributions of the orders  $(e^2)^{3/2}n^{5/2}$  coming from the



**Figure 4.** Low density pressure of hydrogen as a function of  $\Gamma$  for a fixed density. Upper full line– [3]; lower full line– MW [1]; dashes– full expression (16) [26]; dots– Padé approximation [29]; triangles– [30]; squares– PIMC [31]

expansion of Fermi functions, and of  $(ne^2)^{5/2}$  coming from self energy and vertex corrections (see Fig. 3) to the simple random phase approximation of the polarization function which gives, e.g. for the vertex correction to the mean value of the potential energy [25]-[28]

$$\langle V \rangle_{\text{BMW},V} = 3 \frac{(i\hbar)^4}{2} \sum_{ab} \int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}_4 d\mathbf{r}_5 d\mathbf{r}_6 V_{ab}^s(12) V_{ab}(34) V_{bb}(56) \times G_a^0(13) G_a^0(31) G_b^0(25) G_b^0(54) G_b^0(46) G_b^0(62). \quad (21)$$

Results for the hydrogen pressure are shown in Fig. 4 with  $\Gamma = (4\pi n/3)^{1/3} \frac{e^2}{k_B T}$ .

There are statements [24] that the results of the orders  $n^{5/2}$  as derived in the work just cited and given in (16) are in agreement with results of [23] and [24]. However this is doubtful as the assumption of the existence of a  $\xi/6$ -term is not fulfilled.

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