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Coulomb Pair Density Matrix I

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The Coulomb pair density matrix $G_\beta(r, r')$ for attractive and repulsive potentials is not only interesting for determining the two-particle effective potentials, but it is also essential in numerical studies of quantum systems. A high-temperature approximation is obtained for $\log G_\beta(r, r')$, in the form of simple integrals or series expansions; large-distance expansions are also given.

KEY WORDS: Quantum statistical mechanics; elementary processes in plasma.

1. INTRODUCTION

The Coulomb pair density matrix $G_\beta(r, r')$ is not a new subject! Many theoretical and computational studies have been devoted to it. The theoretical papers[1-5] have only dealt with the self term ($r' = r$) and the exchange term ($r' = -r$), in the high- or low-temperature limit and for small or large r. The computational studies[6,7] have of course yielded quantitative and general results, but they need quite heavy means because the function $G_\tau(r, r')$ is expanded on bound and continuum eigenfunctions of the Hamiltonian. Moreover, some difficulties arise from cancellations between various contributions.

Thus it is worthwhile to come back to this subject with the goal of providing general results (whatever r and r' are, for attractive and repulsive potentials) which have to be quantitative (accurate), straightforward (well-converging series or simple integrals), and valid for large domain of temperature. This program would most probably be much too ambitious if it was not for the Coulomb potential. This is in fact weakly singular

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at the origin and it behaves magically with respect to space averaging. Consequently the function $\log G_\beta(r, r')$ is a very well-converging series in the power of the potential and the coefficients (functions of r and r') are quite simple functions which do not depend on the sign of V, while the Hamiltonian spectra are very different in both cases. These functions shall be determined by series expansions or simple integrals from which large-distance expansions are easily obtained.

We will present these various results in several papers. The present one is devoted to the first order. A different method is applied to reach the following orders, and will be presented in a second paper. Finally, a third paper will concern the semiclassical approximation (valid in the low-temperature range) with special emphasis on the question of crossing the turning point on the classical trajectory.

In this paper, devoted then to first order, we first introduce (Section 2) various notations and equations and discuss different behaviors as a function of temperature and distances. In Sections 3–5 the first-order functions are obtained as integrals, series, and asymptotic expansions. The limits for self and exchange terms are considered in each case. In Section 6, this first-order approximation is compared with computational results of Pollock. Finally, Section 7 concerns the integrals of $G_\beta(r, r')$ which arise in virial coefficients.

2. DEFINITIONS AND NOTATIONS

The temperature T is introduced by the time τ,

$$\tau = \beta\hbar = \frac{\hbar}{T} \tag{1}$$

The relative pair density matrix $G_\beta(r, r')$ is defined by

$$G_\tau(r, r') = \langle r | \, e^{-H\tau/\hbar} \, | r' \rangle \tag{2}$$

where H is the two-body Hamiltonian

$$H = -\frac{\hbar^2}{2m} \Delta + V(r) \tag{3}$$

m is the reduced mass ($m_e/2$ for two electrons), and $V(r)$ is the Coulomb potential

$$V(r) = \frac{\alpha}{r}, \qquad \varepsilon_\alpha = \operatorname{sgn}(\alpha) = \pm 1 \tag{4}$$

We shall be concerned with both the repulsive ($\varepsilon_\alpha = 1$) and attractive ($\varepsilon_\alpha = -1$) cases.

If θ denotes the angle between the two vectors r and r', the density matrix $G_\beta(r, r')$ depends only on two independent quantities, which are functions of $|r|$, $|r'|$, and θ. Thus, we introduce the following variables:

$$\mu = \frac{|r-r'|}{2}\left(\frac{2m}{\hbar\tau}\right)^{1/2}, \qquad \nu = \frac{|r|+|r'|}{2}\left(\frac{2m}{\hbar\tau}\right)^{1/2} = g\mu$$
$$g \geqslant 1, \qquad x_m = g^2 - 1 \geqslant 0 \tag{5}$$

$\lambda = [\hbar\tau/(2m)]^{1/2}$ is the thermal de Broglie wavelength.

The quantity g varies from the value 1 for the exchange case ($r' = -r$) to infinity for the direct case ($r' = r$). We shall also use quantities in atomic units, denoted by an asterisk:

$$r^* = r\frac{2m|\alpha|}{\hbar^2}, \qquad \tau^* = \tau\frac{2m\alpha^2}{\hbar^3} \tag{6}$$

For two electrons $r^* = 1$ corresponds to a distance $\hbar^2/m_e e^2 = 0.53$ Å and $\tau^* = 1$ corresponds to a temperature $m_e e^4/\hbar^2 = 27$ eV $= 3.2 \times 10^5$ K.

In the perfect gas limit ($\alpha \to 0$) G_τ tends to G_τ^0,

$$G_\tau^0(r, r') = \left(\frac{m}{2\pi\hbar\tau}\right)^{3/2} e^{-\mu^2} \tag{7}$$

The effective potential $P_\tau(r, r')$ is defined by

$$G_\tau(r, r') = G_\tau^0(r, r')\, e^{-P_\tau(r, r')} \tag{8}$$

and the function $S_\tau(r, r')$ is also introduced:

$$G_\tau(r, r') = e^{-S_\tau(r, r')}, \qquad \frac{S_\tau}{\hbar} = P_\tau + \frac{S_\tau^0}{\hbar}$$
$$S_\tau^0(r, r') = \frac{m}{2\tau}(r-r')^2 + \frac{3}{2}\hbar\log\frac{2\pi\hbar\tau}{m} \tag{9}$$

From the definition (2) for G_τ, there follow the differential equations for $G_\tau(r, r')$, $S_\tau(r, r')$, and $P_\tau(r, r')$:

$$-\partial_\tau G_\tau = \frac{1}{\hbar}\left\{-\frac{\hbar^2}{2m}\Delta + V(r)\right\} G_\tau$$
$$-\partial_\tau S_\tau = \frac{1}{2m}(\nabla S_\tau)^2 - V(r) - \frac{\hbar}{2m}\Delta S_\tau \tag{10}$$
$$\frac{d}{d\tau}P_\tau = \left\{\frac{\partial}{\partial\tau} + \frac{(r-r')}{\tau}\cdot\nabla\right\} P_\tau = -\frac{\hbar}{2m}(\nabla P_\tau)^2 + \frac{1}{\hbar}V(r) + \frac{\hbar}{2m}\Delta P_\tau$$

with the initial condition

$$G_\tau(r, r') \xrightarrow[\tau \to 0]{} \delta(r - r') \tag{11}$$

The equation for S_τ is a diffusion equation (term ΔS_τ) with a "trajectory" term $(\nabla S)^2$ and a "source" term $V(r)$. If the term ΔS_τ is removed, this is the Hamilton–Jacobi equation for the classical action in a potential $-V(r)$. Now if the term $(\nabla S_\tau)^2$ is removed instead of ΔS_τ, this is a diffusion equation with a source term. Thus, we are dealing with a diffusion around the classical trajectory in the potential $-V(r)$. One term is competing with the other one. In the framework of the Feynman path integrals, the term $(\nabla S_\tau)^2$ favors the paths closer to the classical path(s) which minimize(s) the action for the motion from r' to r in time τ, whereas the term ΔS_τ tends to spread out the paths. Various behaviors follow according to the values of r, r', and τ. We shall discuss this point in the next section.

If V does not depend on r, the exact solution is $P_\tau = \tau V/\hbar$. Now for a really r-dependent potential, $\hbar P_\tau/\tau$ will be obtained by averaging the potential twice, once on the trajectory from r' to r and once more around the trajectory because of the diffusion. Thus P_τ is normally a more regular function than $V(r)$. From the special properties of the function $1/r$ in the average process, P_τ is a very smooth function, finite and regular at short distances, and, on the contrary, less convergent than $1/r$ at large distances.

3. THE VARIOUS RANGES OF TEMPERATURES

$\tau^* = 1$ is clearly a boundary between two ranges of temperatures.

3.1. High Temperatures $\tau^* < 1$

In this domain the term $(\nabla P_\tau)^2$ in the equation for P_τ, (10), is always small compared with the others and the only scale of length is $\lambda = [\hbar\tau/(2m)]^{1/2}$. For distances smaller than λ, the diffusion dominates: $\hbar P_\tau/\tau$ is essentially the average of the potential on a volume of the order of λ^3 around the points r and r', and then is of the order of α/λ, which leads to P_τ proportional to $(\tau^*)^{1/2}$. For increasing distances, the average on the previous volume becomes an average on the linear trajectory of the free motion from r' to r during τ. The term $\tau^{-1}(r - r') \cdot \nabla P_\tau$ becomes the dominant term instead of ΔP_τ, and P_τ tends to $\alpha\tau/r$ if $r' = r$, and to $\alpha\tau/|r - r'|$ multiplied by a logarithmic function of the distances in the general case. For $r' = -r$ the diffusion cannot be completely neglected, because the trajectory goes through the center of forces.

For any g, the quantitative measure of the crossover from diffusive to asymptotic behavior is $v^2-\mu^2\sim 1$ or $rr'\cos\theta/2\sim\lambda^2$, which is not equivalent to saying that the minimum distance from the trajectory to the center of forces is of the order of λ. In the general case ($\theta\neq\pi$), P_τ tends exponentially to its asymptotic limit. For $\theta=\pi$ no such transition occurs, because the diffusion does not vanish. The very slow decrease of $|P_\tau|$ at large distances is sizable for the integrals of G_τ; for example, the exchange integral $\int dr\, G_\tau(r,-r)$ is exponentially increasing ($\alpha<0$) or decreasing ($\alpha>0$) as the temperature decreases.

3.2. Low Temperature $\tau^*>1$

Here we have three length scales,

$$\frac{\hbar^2}{2m\,|\alpha|}<\tau^{2/3}\left(\frac{|\alpha|}{2m}\right)^{1/3}<\tau\frac{|\alpha|}{\hbar}\qquad\text{or}\qquad 1<(\tau^*)^{2/3}<\tau^*$$

in atomic units. Let us start with the largest distances, $>\tau\alpha/\hbar$. The terms $(\nabla P_\tau)^2$ and ΔP_τ are small compared with the others. It is the same asymptotic behavior as for high temperatures; $\hbar P_\tau/\tau$ is the average of $V(r)$ on the uniform and linear trajectory from r' to r.

For $r<\tau\alpha/\hbar$, the potential $V(r)$ becomes sizable in the exponential function because βV is larger than 1, but V is not dominant as long as r is larger than $\tau^{2/3}(\alpha/2m)^{1/3}$. The average is always practically the previous one with corrections in α^2, α^3,..., which come from the term $(\nabla P_\tau)^2$ and the diffusion remains negligible. It appears that the lower limit for r does not depend on $\hbar$ and the Kepler's law can be recognized in τ^2 proportional to r^3.

For lower distances, the potential dominates via the term $(\nabla P_\tau)^2$ and the diffusion remains a corrective term. The leading contributions come from the neighborhoods of Kepler trajectories (hyperbola, then ellipse). The time allowed for the path from r' to r becomes enough to explore domains where the value of the potential is smaller in order to decrease the action of the path. It is the semiclassical domain where the term ΔS_τ is treated as a perturbation except near the turning point of the trajectory. The semiclassical approximation is all the more valid since the temperature is smaller. The lower spatial limit is the Bohr radius.

When r is still smaller, all the terms have to be kept. It is the "hard quantum" domain ($\tau^*>1$, $r^*<1$). Nevertheless, it must be observed that the semiclassical value of P_τ for $r^*\sim 1$ tend to the exact value at the origin when the distances decrease just before diverging because of the sudden breakdown of the semiclassical approximation when the distances go to

zero. The leading contributions always come from the neighborhood of the Kepler trajectories, but the "width" of the paths is of the order of r and then is badly evaluated by the semiclassical approximation.

Since the semiclassical approximation remains valid for large distances ($>\tau\alpha/\hbar$), this approximation correctly gives the values of P_τ in all the low-temperature domain except near the origin ($r^* < 1$).

Some limitations have to be expressed for the attractive case because the turning point of the trajectory, which needs a special treatment, is located closer to the origin than in the repulsive case.

By comparing high with low temperatures, it is observed that for $\tau^* < 1$ the potential is never dominant because the time allowed for the path is too small when the diffusion is weak and, when the potential becomes sizable, $\beta V \sim 1$, near the origin, the diffusion is strong. For $\tau^* > 1$, on the contrary, the potential is always dominant as soon as βV is of the order of 1, and the thermal de Broglie wavelength does not appear as a distance scale. Finally we notice that all the boundaries of the various domains cross at the point $\tau^* = r^* = 1$.

4. INTEGRAL SOLUTION FOR HIGH TEMPERATURE

We start from Eq. (10) for P_τ, which we write in the form

$$\left(\frac{d}{d\tau} - \frac{\hbar}{2m}\Delta\right) P_\tau = \frac{1}{\hbar} V(r) - \frac{\hbar}{2m} (\nabla P_\tau)^2, \qquad \frac{d}{d\tau} = \frac{\partial}{\partial\tau} + \frac{r - r'}{\tau} \cdot \nabla \tag{12}$$

This is a diffusion equation in a coordinate system which moves uniformly from r' to r during the time τ. The right-hand side is a source term. From the definition of P_τ, it follows that $P_\tau = 0$ if $V = 0$, $P_\tau = \tau V/\hbar$ if $\nabla V = 0$, and $P_\tau = 0$ as $\tau \to 0$.

Moreover, it is easily shown that the solution of

$$\left(\frac{d}{d\tau} - \frac{\hbar}{2m}\Delta\right) F_\tau(r) = f_\tau(r), \qquad F_{\tau=0} = 0 \tag{13}$$

is

$$F_\tau(r) = \int_0^\tau d\tau_1 \int dr_1 \, f_{\tau_1}\left(r_1 + r' + \frac{\tau_1}{\tau}(r - r')\right) G^0_{\tau_1(\tau-\tau_1)/\tau}(r_1) \tag{14}$$

where G^0_τ is defined by

$$\left(\partial_\tau - \frac{\hbar}{2m}\Delta\right) G^0_\tau(r, r') = 0, \qquad G^0_\tau \xrightarrow[\tau \to 0]{} \delta(r - r')$$
$$G^0_\tau(r, r') = \left(\frac{m}{2\pi\hbar\tau}\right)^{3/2} e^{-(m/2\hbar\tau)(r - r')^2} \tag{15}$$

$F_\tau(r)/\tau$ is obtained by averaging twice the function $f_\tau(r)$. The first average is made on the uniform motion from r' to r during the time τ. The second one is a space average of width $(\hbar\tau/m)^{1/2}$ around the motion. F_τ/τ is then smoother than f_τ.

P_τ is then given by (14) with the r.h.s. of (12) as $f_\tau(r)$. For a regular potential, it is sensible to look at an expansion in powers of V, by solving iteratively the equation and beginning with $V(r)/\hbar$ for the first $f_\tau(r)$. The first-order solution is then $P_\tau = P_\tau^{(1)}$:

$$P_\tau^{(1)}(r, r') = \frac{1}{\hbar}\int_0^\tau d\tau_1 \int dr_1\, V\left(r_1 + r' + \frac{\tau_1}{\tau}(r - r')\right) G^0_{\tau_1(\tau-\tau_1)/\tau}(r_1) \quad (16)$$

By taking the integral

$$\int dr_1 \frac{1}{|r_1 + r_0|}\frac{1}{(\pi a)^{3/2}} e^{-r_1^2/a} = \frac{1}{r_0}\operatorname{erf}\left(\frac{r_0}{\sqrt{a}}\right) \quad (17)$$

(erf = error function) into account, we get

$$P_\tau^{(1)}(r, r') = \frac{\alpha}{\hbar}\int_0^\tau d\tau_1 \frac{1}{|r' + (\tau_1/\tau)(r - r')|}\operatorname{erf}\frac{|r' + (\tau_1/\tau)(r - r')|}{[2\hbar\tau_1(\tau - \tau_1)/m\tau]^{1/2}} \quad (18)$$

We shall transform this expression into two other integrals which exhibit explicitly the dependence of P_τ on only two space quantities (μ, g) or (μ, ν). Moreover, these new expressions will allow us to obtain $P_\tau^{(1)}$ as a series.

First we introduce I,

$$P_\tau^{(1)}(r, r') = \varepsilon_\alpha(\tau^*)^{1/2} I(\mu, g) \quad (19)$$

which will then depend on only two variables. With the help of

$$h = \frac{|r| - |r'|}{|r - r'|}, \quad |h| < 1, \qquad g = \frac{\nu}{\mu} = \frac{|r| + |r'|}{|r - r'|} \geqslant 1, \qquad \lambda = \frac{2\tau_1 - \tau}{\tau} \quad (20)$$

we calculate $|r' + \tau_1(r - r')/\tau|$ in (18) and obtain for I

$$I = \frac{1}{2\mu}\int_{-1}^{+1} \frac{d\lambda}{(\lambda^2 + 2\lambda gh + g^2 + h^2 - 1)^{1/2}} \operatorname{erf}\left(\mu\left(\frac{\lambda^2 + 2\lambda gh + g^2 + h^2 - 1}{1 - \lambda^2}\right)^{1/2}\right) \quad (21)$$

By integrating over x,

$$x = \frac{\lambda^2 + 2\lambda gh + g^2 + h^2 - 1}{1 - \lambda^2} \quad (22)$$

instead of λ, we shall prove that I does not depend on h. The derivative of x with respect to λ,

$$\frac{1}{x}\frac{dx}{d\lambda}=2\frac{\lambda^2 gh+\lambda(g^2+h^2)+gh}{(1-\lambda^2)(\lambda^2+2\lambda gh+g^2+h^2-1)} \tag{23}$$

shows that x decreases from $+\infty$ for $\lambda=-1$ to a minimum $x_m=g^2-1$ for $\lambda=-h/g$ and then increases again to $+\infty$ for $\lambda=+1$. The other root of the denominator of (23), $\lambda=-g/h$, gives $x=x_M=h^2-1<0$ and is not in the integrating interval.

It is easily shown that

$$\begin{gathered}(x-x_m)^{1/2}=\frac{|\lambda g+h|}{(1-\lambda^2)^{1/2}}, \qquad (x-x_M)^{1/2}=\frac{\lambda h+g}{(1-\lambda^2)^{1/2}} \\ ((x-x_m)(x-x_M))^{1/2}=\frac{|\lambda^2 gh+\lambda(g^2+h^2)+gh|}{1-\lambda^2}\end{gathered} \tag{24}$$

and it follows that

$$\begin{gathered}\frac{d\lambda}{(\lambda^2+2\lambda gh+g^2+h^2-1)^{1/2}}=\pm dx\frac{(1-\lambda^2)^{1/2}}{2[x(x-x_m)(x-x_M)]^{1/2}} \\ \pm=\operatorname{sgn}\left(\lambda+\frac{h}{g}\right)\end{gathered} \tag{25}$$

In order to bring together the contributions of the two domains $(-1, -h/g)$ and $(-h/g, +1)$, we have to calculate $(1-\lambda_1^2)^{1/2}+(1-\lambda_2^2)^{1/2}$, where λ_1 and λ_2 are the two roots of (22) which give the same x. From (24) we deduce

$$\begin{aligned}(1-\lambda_1^2)^{1/2}+(1-\lambda_2^2)^{1/2}&=\frac{1}{(x-x_M)^{1/2}}\{(\lambda_1+\lambda_2)h+2g\} \\ &=\frac{2g}{1+x}(x-x_M)^{1/2}\end{aligned} \tag{26}$$

by taking into account that the sum $\lambda_1+\lambda_2$ is $-2gh/(1+x)$ [from (22)]. Finally $I(\mu, g)$ is obtained as an integral over x,

$$I(\mu, g)=\frac{g}{2\mu}\int_{x_m}^{+\infty}\frac{dx}{(1+x)[x(x-x_m)]^{1/2}}\operatorname{erf}(\mu\sqrt{x}), \qquad x_m=g^2-1 \tag{27}$$

which explicitly depends on only two variables.

Another transformation will be useful for obtaining the series expansion of I. In (27) we write the error function as

$$\operatorname{erf}(u)=\frac{2u}{\sqrt{\pi}}\int_0^1 dz\, e^{-z^2u^2} \tag{28}$$

set $x=x_m+(v^2/z^2\mu^2)$, and integrate first over v:

$$I(\mu, g)=\sqrt{\pi}\int_0^1 dz\, e^{z^2\mu^2}\frac{2}{\pi}\int_0^{+\infty} dv\,\frac{e^{-v^2}}{v^2+z^2v^2}\,zve^{-z^2v^2} \tag{29}$$

With the well-known integral representation for $\operatorname{erfc}(t)$[8]

$$\operatorname{erfc}(t)=\frac{2}{\pi}te^{-t^2}\int_0^{+\infty}\frac{dv}{v^2+t^2}e^{-v^2} \tag{30}$$

I is easily obtained in variables (μ, v)

$$I(\mu, v)=\sqrt{\pi}\int_0^1 dz\, e^{\mu^2z^2}\operatorname{erfc}(vz) \tag{31}$$

In the self case ($\mu=0$), integrating by parts (31) leads to

$$I_S(v)=I(\mu=0, v)=\frac{1-e^{-v^2}}{v}+\sqrt{\pi}\operatorname{erfc}(v) \tag{32}$$

which is the result of Kelbg.[9] In the exchange case ($g=1$), integrating by parts (27) gives

$$I_E(\mu)=I(\mu, g=1)=\frac{1}{2\sqrt{\pi}}\int_0^{+\infty}\frac{dx}{\sqrt{x}}\log\frac{1+x}{x}e^{-\mu^2x} \tag{33}$$

For any g, a similar expression can be obtained always by integrating (27) by parts and taking account of

$$\frac{d}{dx}\log\frac{g\sqrt{x}+(x-x_m)^{1/2}}{g\sqrt{x}-(x-x_m)^{1/2}}=\frac{g}{(x+1)[x(x-x_m)]^{1/2}}, \qquad x_m=g^2-1 \tag{34}$$

$$I(\mu, g)=\frac{1}{2\mu}\log\frac{g+1}{g-1}-\frac{1}{2\sqrt{\pi}}\int_{x_m}^{+\infty}\frac{dx}{\sqrt{x}}\log\frac{g\sqrt{x}+(x-x_m)^{1/2}}{g\sqrt{x}-(x-x_m)^{1/2}}e^{-\mu^2x} \tag{35}$$

which was first mentioned by Ceperley[10] and which will be useful for obtaining the asymptotic expansion of I for large μ.

5. SERIES EXPANSION FOR *I*

Here we derive the series expansion for I. By setting the series expansions of $e^{\mu^2 z^2}$ and $\operatorname{erfc}(vz)$,

$$\operatorname{erfc}(v) = 1 - \frac{2}{\sqrt{\pi}} \sum_{m \geqslant 0} (-1)^m \frac{v^{2m+1}}{m!\,(2m+1)} \tag{36}$$

in (31) and integrating on z, we obtain $I(\mu, v)$,

$$I(\mu, v) = \sqrt{\pi} \sum_{n \geqslant 0} \frac{\mu^{2n}}{n!\,(2n+1)} - v \sum_{\substack{n \geqslant 0 \\ m \geqslant 0}} (-1)^m \frac{\mu^{2n} v^{2m}}{n!\,m!\,(2m+1)(n+m+1)} \tag{37}$$

The second series can be transformed by taking the variables μ and $x_m = g^2 - 1$. We set $v^2 = \mu^2(1 + x_m)$ and take together the terms with the same power of μ; the coefficient of μ^{2p} appears as a polynomial of degree p in x_m,

$$\frac{1}{p+1} \sum_{q=0}^{p} (-1)^q \frac{x_m^q}{q!} \frac{1}{2} \sum_{n=0}^{p-q} \frac{(-1)^n}{n!\,(p-q-n)!\,(n+q+1/2)} \qquad (p \geqslant 0) \tag{38}$$

By using the identity

$$\sum_{n=0}^{w} \frac{(-1)^n}{n!\,(w-n)!\,(n+z)} = \frac{\Gamma(z)}{\Gamma(w+1+z)} \tag{39}$$

for $z = q + \frac{1}{2}$, $w = p - q$, it follows that

$$I(\mu, g) = \sqrt{\pi} \sum_{n \geqslant 0} \frac{\mu^{2n}}{n!\,(2n+1)} - g\mu \sum_{p \geqslant 0} \mu^{2p} \frac{\Gamma(3/2)}{(p+1)\,\Gamma(p+3/2)} \sum_{q=0}^{p} (-1)^q \frac{x_m^q}{q!} \frac{\Gamma(q+1/2)}{\Gamma(1/2)} \tag{40}$$

This expression can be obtained from (27) and the polynomials come from the large-x expansion of $1/(x+1)[x(x-x_m)]^{1/2}$; the calculations are rather heavy and we shall not give any details. These polynomials appear as a truncated series, so that the numerical calculation of the series (40) is easily done; the polynomial of order $p+1$ is obtained by a simple addition to the polynomial of order p. $I(\mu, g)$ is the difference between two converging series of μ. The first one does not depend on g. Each series increases as e^{μ^2}/μ^2 for increasing μ, but the difference tends well to zero.

Let us consider the two limiting cases $g \to \infty$ and $g \to 1$. In the self case $\mu \to 0$ with $g\mu = v$ fixed, it follows that

$$I_S(v) = \sqrt{\pi} - \sum_{m \geq 0} (-1)^m \frac{v^{2m+1}}{(m+1)!\,(2m+1)} \tag{41}$$

which can be obtained directly from (32). Now in the exchange case $x_m \to 0$ all the polynomials tend to 1 and the series for I_E is

$$I_E(\mu) = \sqrt{\pi} \sum_{n \geq 0} \frac{\mu^{2n}}{n!\,(2n+1)} - \sum_{p \geq 0} \mu^{2p+1} \frac{\Gamma(3/2)}{(p+1)\,\Gamma(p+3/2)} \tag{42}$$

6. ASYMPTOTIC EXPANSIONS

For large value of μ, $I(\mu, g)$ exponentially tends to a simple expression (except for $g = 1$). It is in fact easily seen that the contributions to the integral (35) arise from x such that $x - x_m$ is of the order of $1/\mu^2$ and the integral tends to zero as $\exp(-\mu^2 x_m)$ for large μ. $I(\mu, g)$ well tends exponentially to the first term. The expansion of $I(\mu, g)$ can be obtained by expanding the logarithm for $(x - x_m)^{1/2} \ll g\sqrt{x}$. We set $x = x_m + t/\mu^2$ and obtain

$$I(\mu, g) = \frac{1}{2\mu} \log \frac{g+1}{g-1} - \frac{1}{\sqrt{\pi}} \frac{e^{-\mu^2 x_m}}{\mu} \sum_{p \geq 0} \frac{1}{(2p+1)\, g^{2p+1} (\mu^2 x_m)^{p+1}} \times \int_0^{+\infty} dt\, e^{-t} t^{p+1/2} \left(1 + \frac{t}{\mu^2 x_m}\right)^{-(p+1)} \tag{43}$$

We expand again $(1 + t/\mu^2 x_m)^{-(p+1)}$ in series of t, integrate over t, and bring together the terms of the same power of $\mu^2 x_m$:

$$\begin{aligned} I(\mu, g) &\simeq \frac{1}{2\mu} \log \frac{g+1}{g-1} - \frac{e^{-\mu^2 x_m}}{2\mu g} \sum_{q \geq 0} (-1)^q \frac{\Gamma(q+3/2)}{\Gamma(3/2)} \frac{1}{(\mu^2 x_m)^{q+1}} \\ &\quad \times \sum_{p=0}^{q} (-1)^p \frac{q!}{(2p+1)\, p!\, (q-p)!} \frac{1}{g^{2p}} \\ &\sim \frac{1}{2\mu} \log \frac{g+1}{g-1} - \frac{e^{-\mu^2 x_m}}{2\mu g} \left\{ \frac{1}{\mu^2 x_m} - \frac{3}{2} \frac{1}{(\mu^2 x_m)^2} \left(1 - \frac{1}{3g^2}\right) \right. \\ &\quad \left. + \frac{\cdot 15}{4} \frac{1}{(\mu^2 x_m)^3} \left(1 - \frac{2}{3g^2} + \frac{1}{5g^4}\right) + \cdots \right\}, \qquad (\mu^2 x_m \gtrsim 1) \end{aligned} \tag{44}$$

This is clearly an asymptotic expansion (in the mathematical meaning). It gives a good evaluation of I as soon as $\mu^2 x_m$ is larger than 1.

The term with $\exp(-\mu^2 x_m)$ occurs from diffusion. In the limit $|r-r'| \gg \lambda$, G^0 in (16) can be set equal to a Dirac function. $P_\tau^{(1)}(r, r')$ is then only the average of the potential on the uniform motion from r' to r; a straightforward calculation gives

$$P_\tau^{(1)}(r, r') \sim \frac{1}{\hbar}\int_0^\tau d\tau_1\, V\left(r' + \frac{\tau_1}{\tau}(r-r')\right) = \varepsilon_\alpha(\tau^*)^{1/2}\frac{1}{2\mu}\log\frac{g+1}{g-1} \tag{45}$$

The diffusion effects decrease exponentially as soon as $\mu^2 x_m = \mu^2 - \nu^2$ exceeds unity.

In the self case $g \to \infty$, the expression (44) is simplified, $\mu^2 x_m$ tends to ν^2, the polynomials in $1/g$ tend to 1, and the first term tends to $1/g\mu = 1/\nu$:

$$I_S(\nu) \simeq \frac{1}{\nu} - \frac{1}{2}e^{-\nu^2}\sum_{q\geqslant 0}(-1)^q\frac{\Gamma(q+3/2)}{\Gamma(3/2)}\frac{1}{\nu^{2q+3}} \sim \frac{1}{\nu} - \frac{e^{-\nu^2}}{2\nu^3} \qquad (\nu \gtrsim 1) \tag{46}$$

Of course this result can be directly derived from (32).

In the exchange case $g \to 1$, $x_m \to 0$, we start from (33) and set $x = t/\mu^2$; $\log(1+x)/x$ is equal to $\log\mu^2 - \log t + \log(1 + t/\mu^2)$; integration of the first two terms is done with Euler's functions; the last term is expanded in power of t/μ^2; it follows that

$$\begin{aligned} I_E(\mu) &\simeq \frac{1}{\mu}\left\{\log(2\mu) + \frac{1}{2}\gamma\right\} + \frac{1}{4}\sum_{q\geqslant 0}\frac{(-1)^q}{q+1}\frac{\Gamma(q+3/2)}{\Gamma(3/2)}\frac{1}{\mu^{2q+3}} \\ &\sim \frac{1}{\mu}\left\{\log(2\mu) + \frac{1}{2}\gamma\right\} + \frac{1}{4\mu^3} \qquad (\mu \gtrsim 1) \end{aligned} \tag{47}$$

where γ is Euler's constant. $I_E(\mu)$ is a very slowly decreasing function for large μ which plays an important part when calculating integrals of $G_\tau(r, -r)$.

7. COMPARISON WITH NUMERICAL RESULTS

Before comparing with the exact numerical results of Pollock,[7] we point out some properties of $I(\mu, g)$. When all distances vanish ($\forall g$), I tends to $\sqrt{\pi}$. The value of $P_\tau(r, r')$ at the origin is exactly known as an integral or a series in powers of $(\tau^*)^{1/2}$.[7] $\sqrt{\pi}$ is the exact value of the coefficient of $(\tau^*)^{1/2}$; the following term is $\tau^*\pi(1-\pi/3)/2 \approx -0.07\tau^*$. It appears that it is an upper bound of the error (for finite μ, the error is less). Then the approximation $P_\tau(r, r') \sim \varepsilon_\alpha(\tau^*)^{1/2} I(\mu, g)$ is valid within 7% for $\tau^* \leqslant 1$ ($\forall\mu$ and g).

The variations of I are very regular; I decreases with μ for fixed g and decreases with g for fixed μ.

Table I. Comparison of the Present Approximation with Exact Value of P_τ from Pollock in the Direct and Exchange Cases ($\tau^* = 1$)

	$P_\tau(r^*, r^*)$		$P_\tau(r^*, -r^*)$	
r^*	$I(\mu = 0, \nu = r^*)$	Pollock	$I(\mu = r^*, \nu = r^*)$	Pollock
0	1.772 45	1.703 78	1.772 45	1.703 78
0.2	1.573 78	1.505 88	1.593 68	1.528 42
0.5	1.292 29	1.232 07	1.387 33	1.332 14
0.7	1.124 47	1.073 47	1.279 00	1.230 59
1.0	0.910 93	0.875 58	1.147 24	1.107 64
1.5	0.656 48	0.641 19	0.983 47	0.954 77
2.0	0.499 13	0.493 25	0.864 40	0.843 00
2.5	0.399 95	0.397 55	0.773 77	0.757 25
3.0	0.333 33	0.332 21	0.702 06	0.689 14

In Table I we compare the exact value of P_τ from Pollock with the present approximation for $\varepsilon_\alpha = 1$, $\tau^* = 1$, in the two cases $g \to \infty$ and $g = 1$. It is easily seen that the approximation is improved with increasing μ. We also give (Table II) results from series and asymptotic expansions with only a few terms in each case. The two expansions agree for intermediate distances.

Table II. Values Obtained by Two-Term and Ten-Term Expansions

	$I(\mu = 0, \nu = r^*)$		$I(\mu = r^*, \nu = r^*)$	
r^*	Series [Eq. (41)][a]	Asymptotic [Eq. (46)][b]	Series [Eq. (42)][a]	Asymptotic [Eq. (47)][b]
0	1.772 45	—	1.772 45	—
0.50	1.292 29	—	1.387 33	—
1.0	0.910 93	0.816 06	1.147 24	1.044 26
1.5	0.656 48	0.651 05	0.983 46	0.974 20
2.0	0.501 04	0.498 86	0.859 21	0.862 84
2.5	—	0.399 94	—	0.773 30
3.0	—	0.333 33	—	0.701 94

[a] Ten terms.
[b] Two terms.

8. VIRIAL COEFFICIENTS

The thermodynamic functions of Coulomb fluids cannot be expanded in powers of the density as for fluids with short-range forces. Nevertheless integrals of $G_\tau(r, \pm r)$ also appear in coefficients of the specific expansions for Coulomb fluids.[11] Here we evaluate these integrals within our approximation for $\tau^* \leqslant 1$ and compare with known results. We deal separately with the two cases (exchange and self).

8.1. Exchange

We want to calculate

$$q_E(\tau^*) = \int dr\, G_\tau(r, -r) = \tfrac{1}{8} e^{-\psi_E(\tau^*)} \tag{48}$$

with

$$G_\tau(r, -r) \simeq \left(\frac{m}{2\pi\hbar\tau}\right)^{3/2} \exp[-\mu^2 - \varepsilon_\alpha(\tau^*)^{1/2} I_E(\mu)] \tag{49}$$

The value 1/8 is the perfect gas limit ($\tau^* = 0$). As for P_τ, we shall calculate the first term in the expansion of ψ_E in power of τ^* by expanding $\exp[-\varepsilon_\alpha(\tau^*)^{1/2} I_E]$ to first order in $(\tau^*)^{1/2}$. It follows that

$$\psi_E \simeq \varepsilon_\alpha(\tau^*)^{1/2} \frac{4}{\pi} \int_0^{+\infty} \mu^2\, d\mu\, e^{-\mu^2} I_E(\mu) \tag{50}$$

We take the integral (33) for I_E, and set $x = t^2/\mu^2$; we integrate by parts over μ in order to remove the logarithm:

$$\psi_E \simeq \varepsilon_\alpha(\tau^*)^{1/2} \frac{4}{\pi} \int_0^{+\infty} dt \int_0^{+\infty} d\mu\, e^{-(t^2+\mu^2)} \frac{\mu}{\mu^2 + t^2} \tag{51}$$

This integral is easily evaluated in polar coordinates and we find

$$\psi_E \simeq \frac{2}{\sqrt{\pi}} \varepsilon_\alpha(\tau^*)^{1/2} \tag{52}$$

For $\tau^* = 1$, $\exp(\pm 2/\sqrt{\pi})$ are 3.09 and 0.324, respectively. The second value (repulsive potential) is to be compared with the exact value 0.340 by Jancovici[3] [$e^{-\psi_E}$ is $8A$, where A is the integral (38) in the appendix of that paper]. For the attractive case a more precise value is 3.29, as we shall

see in a forthcoming paper. It is to be noticed that q_E is a really decreasing (increasing) exponential function for repulsive (attractive) potential. We also observe that the first-order calculation of ψ_E gives a good evaluation for q_E in the domain $\tau^* < 1$.

8.2. Self

As $P_\tau(r, r')$ behaves as $1/r$ at large distances, it is necessary to subtract from $G_\tau(r, r)$ all the terms which decrease slower than $1/r^3$ before integrating on r,[11]

$$q_S(\tau^*) = \int dr\, [G_\tau(r, r) - G_\tau^{(AS)}(r, r)] \tag{53}$$

We calculate q_E to first order by setting $1 - \varepsilon_\alpha(\tau^*)^{1/2} I_S(v)$ for $e^{-P_1(r,r)}$. As $I_S(v)$ tends exponentially to $1/v$, we obtain

$$q_S(\tau^*) = -\frac{\varepsilon_\alpha(\tau^*)^{1/2}}{2\pi} \int_0^{+\infty} v^2\, dv \left[I_S(v) - \frac{1}{v} \right] \tag{54}$$

I_S is given by (32). Integrating by parts over v yields

$$q_S(\tau^*) \simeq \frac{\varepsilon_\alpha(\tau^*)^{1/2}}{12\sqrt{\pi}} \tag{55}$$

We notice that the sign of q_S follows from the subtracted term $1/v$. The contribution to the pressure proportional to $-q_S$ has the sign of $-\varepsilon_\alpha$.

We also mention that the two expansions of $q_E(\tau^*)$ and $q_S(\tau^*)$ in power of $(\tau^*)^{1/2}$ coincide with the results of Kraeft *et al.*[12]

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