

EXCHANGE QUANTUM CORRECTIONS IN THE ONE-COMPONENT PLASMA

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The leading term of the exchange quantum correction to the free energy of a dense one-component plasma is computed in the near-classical limit. Two-body exchange is dominant. The path-integral method is used in its semi-classical limit. The exchange free energy is found to be exponentially small.

1. Introduction

The one-component plasma, also called “jellium”, is a system of identical particles of charge e and mass M embedded in a uniform neutralizing background of opposite charge. This model, which has been shown to be well-behaved¹⁾, is believed to provide a good description of certain stellar interiors, where the nuclei are the particles and the sea of degenerate electrons forms the background. The equilibrium properties of the one-component plasma have been extensively studied by computer simulation^{2,3)}, in the case when classical statistical mechanics is valid. Quantum effects, when they are small enough, can be added as corrections and computed⁴⁾ by a Wigner–Kirkwood expansion in powers of \hbar^2 . Exchange quantum effects, however, are not taken into account by the Wigner–Kirkwood method. It has been qualitatively argued⁴⁾ that the exchange quantum corrections are negligible compared to the direct quantum corrections. In the present paper, we compute the leading term of the exchange correction to the free energy in the near-classical limit, and show that this exchange term is indeed exponentially small.

The state of the plasma is defined by the number density ρ and the temperature T , or equivalently the ion-sphere radius $a = (3/4\pi\rho)^{1/3}$ and the two-body average classical distance of closest approach βe^2 (where $\beta = 1/k_B T$). A convenient classical dimensionless coupling parameter is $\Gamma = \beta e^2/a$. Quantum effects depend on the thermal de Broglie wavelength $\lambda = (2\pi\hbar^2\beta/M)^{1/2}$, where M is the mass of a particle. We are interested here in the

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near-classical case where λ is small enough compared to the other lengths a and βe^2 (note that the condition $\lambda \ll \beta e^2$ is a *low-temperature* requirement), but no restriction is made about the value of the coupling parameter Γ , which is large for the interesting dense matter situations encountered in astrophysics.

In section 2, the statistical mechanical problem is reduced to a one-body calculation, which is performed in section 3 by path-integral techniques. The result is discussed in section 4.

2. Two-body exchange free energy

We consider a system of N particles of spin s in a volume Ω ($\rho = N/\Omega$). Let H be the hamiltonian. The total free energy F is given by⁵

$$\beta F = -\ln \left[\frac{1}{N!} \int \left(\langle \mathbf{r}_1 \mathbf{r}_2 \mathbf{r}_3 \dots \mathbf{r}_N | \exp(-\beta H) | \mathbf{r}_1 \mathbf{r}_2 \mathbf{r}_3 \dots \mathbf{r}_N \rangle \right. \right. \\ \left. \left. \pm \frac{N(N-1)}{2(2s+1)} \langle \mathbf{r}_1 \mathbf{r}_2 \mathbf{r}_3 \dots \mathbf{r}_N | \exp(-\beta H) | \mathbf{r}_2 \mathbf{r}_1 \mathbf{r}_3 \dots \mathbf{r}_N \rangle + \dots \right) d\mathbf{r}_1 \dots d\mathbf{r}_N \right], \quad (1)$$

where the upper (lower) sign refers to bosons (fermions). In (1) we have kept only the two-body exchange term; it will be shown in section 4 that exchanges involving more than two particles give only higher-order corrections. Furthermore, since the two-body exchange term is itself a correction, we can expand the logarithm in (1) with respect to that term and we obtain

$$F = F_d + F_{\text{ex}}, \quad (2)$$

where the direct part of the free energy is given by

$$\beta F_d = -\ln \left(\frac{1}{N!} \int \langle \mathbf{r}_1 \mathbf{r}_2 \mathbf{r}_3 \dots \mathbf{r}_N | \exp(-\beta H) | \mathbf{r}_1 \mathbf{r}_2 \mathbf{r}_3 \dots \mathbf{r}_N \rangle d\mathbf{r}_1 \dots d\mathbf{r}_N \right), \quad (3)$$

and the exchange part by

$$\beta F_{\text{ex}} = \mp \frac{N(N-1)}{2(2s+1)} \frac{\int \langle \mathbf{r}_1 \mathbf{r}_2 \mathbf{r}_3 \dots \mathbf{r}_N | \exp(-\beta H) | \mathbf{r}_2 \mathbf{r}_1 \mathbf{r}_3 \dots \mathbf{r}_N \rangle d\mathbf{r}_1 \dots d\mathbf{r}_N}{\int \langle \mathbf{r}_1 \mathbf{r}_2 \mathbf{r}_3 \dots \mathbf{r}_N | \exp(-\beta H) | \mathbf{r}_1 \mathbf{r}_2 \mathbf{r}_3 \dots \mathbf{r}_N \rangle d\mathbf{r}_1 \dots d\mathbf{r}_N}. \quad (4)$$

We are interested in the behaviour of (4) in the small λ limit. Therefore, we can replace the integral in the denominator by its classical limit Q/λ^{3N} , where Q is the classical configuration integral. In order to study the matrix element in the numerator, it is convenient to rewrite it with a slightly different notation as

$$\mathcal{N}(\mathbf{r}_1^0, \dots, \mathbf{r}_N^0) = \langle \mathbf{r}_1^0 \mathbf{r}_2^0 \mathbf{r}_3^0 \dots \mathbf{r}_N^0 | \exp(-\beta H) | \mathbf{r}_2^0 \mathbf{r}_1^0 \mathbf{r}_3^0 \dots \mathbf{r}_N^0 \rangle, \quad (5)$$

using r_i^0 to denote some c -number value of a position and saving the notation r_i for the corresponding operator. The hamiltonian may be split as

$$H = - \sum_{i=1}^N (\hbar^2/2M)\Delta_i + e^2/r_{12} + W(\mathbf{r}_{12}, \mathbf{R}_{12}, \mathbf{r}_3, \dots, \mathbf{r}_N), \quad (6)$$

where W is the total potential energy minus its explicitly written e^2/r_{12} term; for convenience the positions of particles 1 and 2 are described in (6) by the relative and center-of-mass coordinates $\mathbf{r}_{12} = \mathbf{r}_2 - \mathbf{r}_1$ and $\mathbf{R}_{12} = (\mathbf{r}_1 + \mathbf{r}_2)/2$. When looking for the leading term of (5) in the near-classical limit, it is enough to take into account the quantum effects only for the relative motion of those particles 1 and 2 which are exchanged; therefore, we can replace in (6) the operators $\mathbf{R}_{12}, \mathbf{r}_3, \dots, \mathbf{r}_N$ by $\mathbf{R}_{12}^0, \mathbf{r}_3^0, \dots, \mathbf{r}_N^0$. Furthermore, since the off-diagonal range of \mathcal{N} goes to zero in the classical limit, near that limit we can replace \mathbf{r}_{12} by 0 in the function W which is smooth around $\mathbf{r}_{12} = 0$. Thus, W is approximated by a c -number, the contribution of which to (5) can be factorized out.

The contributions to (5) of the kinetic energies of particles 3 to N and of the center of mass of particles 1 and 2 can also be factorized. We obtain

$$\mathcal{N}(\mathbf{r}_1^0, \dots, \mathbf{r}_N^0) = (2\sqrt{2}/\lambda^{3N-3}) \exp[-\beta W(0, \mathbf{R}_{12}^0, \mathbf{r}_3^0, \dots, \mathbf{r}_N^0)] \\ \times \langle \mathbf{r}_{12}^0 | \exp\{-\beta[-(\hbar^2/M)\Delta_{12} + e^2/r_{12}]\} | \mathbf{r}_{12}^0 \rangle, \quad (7)$$

where Δ_{12} is the laplacian with respect to the relative coordinate \mathbf{r}_{12} . Using the expression (7) of (5) in (4) gives

$$\frac{\beta F_{\text{ex}}}{N} = \mp \rho \frac{2\sqrt{2}\lambda^3}{2(2s+1)} e^C \int \langle \mathbf{r}^0 | \exp\{-\beta[-(\hbar^2/M)\Delta + e^2/r]\} | \mathbf{r}^0 \rangle d\mathbf{r}^0, \quad (8)$$

where the relative coordinate \mathbf{r}_{12} has been renamed \mathbf{r} for simplicity; the constant C is defined by

$$\rho^2 e^C = \frac{N(N-1)}{Q} \int \exp[-\beta W(0, \mathbf{R}_{12}^0, \mathbf{r}_3^0, \dots, \mathbf{r}_N^0)] d\mathbf{r}_3^0 \dots d\mathbf{r}_N^0 \quad (9)$$

and is therefore related to the short-distance behaviour of the classical pair correlation function $g_c(r)$ by

$$g_c(r) = \exp[-\beta e^2/r + C + \dots]. \quad (10)$$

A numerical fit for C as a function of Γ has been given in ref. 6 (C is of the order of Γ).

Through (8), the evaluation of the exchange free energy is reduced to a one-body problem involving the thermal Green's function of a particle in a Coulomb potential.

3. Path-integral calculation

The integral in (8) upon the thermal Green's function

$$G(\mathbf{r}', \mathbf{r}''; \beta) = \langle \mathbf{r}' | \exp\{-\beta[-(\hbar^2/M)\Delta + e^2/r]\} | \mathbf{r}'' \rangle \quad (11)$$

can be evaluated by manipulations on special functions, as described in the Appendix. Here, we prefer to use path-integral techniques⁵⁾ which shed more light on the validity of the approximations which have been made.

The matrix element in (8) has the path-integral representation

$$G(\mathbf{r}^0, -\mathbf{r}^0; \beta) = \int \mathcal{D}\mathbf{r} \exp\left(-\hbar^{-1} \int_0^{\beta\hbar} [(M/4)\dot{\mathbf{r}}^2 + e^2/r] dt\right), \quad (12)$$

where the functional integral has to be taken on all paths $\mathbf{r}(t)$ which go from $-\mathbf{r}^0$ to \mathbf{r}^0 in a "time" $\beta\hbar$. In the near-classical limit, eq. (12) is dominated by the paths which minimize

$$S(-\mathbf{r}^0, \mathbf{r}^0; \beta\hbar) = \int_0^{\beta\hbar} [(M/4)\dot{\mathbf{r}}^2 + e^2/r] dt. \quad (13)$$

S is the classical action for a particle of mass $M/2$ moving in the reversed potential $-e^2/r$, and is minimum along a classical trajectory obeying Kepler's laws. Furthermore, the integral upon \mathbf{r}^0 ,

$$A = \int G(\mathbf{r}^0, -\mathbf{r}^0; \beta) d\mathbf{r}^0, \quad (14)$$

is dominated by the value of \mathbf{r}^0 which minimizes the action considered as a function of \mathbf{r}^0 . Thus,

$$\left(\frac{\partial S(\mathbf{r}', \mathbf{r}''; \beta\hbar)}{\partial \mathbf{r}'} + \frac{\partial S(\mathbf{r}', \mathbf{r}''; \beta\hbar)}{\partial \mathbf{r}''}\right)_{-\mathbf{r}' = \mathbf{r}'' = \mathbf{r}^0} = 0. \quad (15)$$

Since

$$\frac{\partial S(\mathbf{r}', \mathbf{r}''; t)}{\partial \mathbf{r}'} = -\mathbf{p}'; \quad \frac{\partial S(\mathbf{r}', \mathbf{r}''; t)}{\partial \mathbf{r}''} = \mathbf{p}'', \quad (16)$$

where \mathbf{p}' and \mathbf{p}'' are the momenta at the end-points \mathbf{r}' and \mathbf{r}'' , eq. (15) means that these momenta are opposite. Therefore the trajectories are half-circles (fig. 1); the radius is easily found to be

$$\sigma = (2\hbar^2\beta^2 e^2/\pi^2 M)^{1/3}, \quad (17)$$

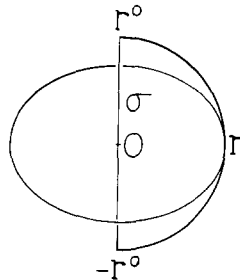


Fig. 1. A dominant trajectory for two-particle exchange.

the momentum along the trajectory has the constant magnitude

$$p = (\pi M^2 e^2 / 4 \hbar \beta)^{1/3}. \quad (18)$$

and the action is

$$S = \frac{3}{2} (\pi^2 \hbar \beta e^4 M / 2)^{1/3}. \quad (19)$$

This means that (14) is dominated by a factor $\exp(-S/\hbar)$, with S given by (19).

There is however an infinity of classical trajectories obtained from one another by rotations around the axis which goes through $-\mathbf{r}^0$, the origin, and \mathbf{r}^0 . The usual semi-classical approximation^{7,8)},

$$G(\mathbf{r}', \mathbf{r}''; \beta) = (2\pi\hbar)^{-d/2} \left(\det \left| -\frac{\partial^2 S(\mathbf{r}'', \mathbf{r}'; \beta\hbar)}{\partial r'_\alpha \partial r''_\beta} \right| \right)^{1/2} \exp\left(-\frac{1}{\hbar} S(\mathbf{r}'', \mathbf{r}'; \beta\hbar)\right) \quad (20)$$

(where d is the number of dimensions and where the indices α, β denote cartesian components) comes from keeping only the paths in the neighborhood of one extremal one⁹⁾. If applied directly to $G(\mathbf{r}^0, -\mathbf{r}^0; \beta)$, eq. (20) would give a divergent answer because of the rotational degeneracy. The above difficulty may be circumvented by writing

$$G(\mathbf{r}^0, -\mathbf{r}^0; \beta) = \int G(\mathbf{r}^0, \mathbf{r}; \beta/2) G(\mathbf{r}, -\mathbf{r}^0; \beta/2) d\mathbf{r}. \quad (21)$$

The integral in (21) is dominated by contributions from \mathbf{r} in the neighborhood of the equatorial circle; integration along that circle will take care of the rotational degeneracy. It is now possible to use the approximation (20) for the Green's functions in the right-hand side of (21). When \mathbf{r} is on the equatorial circle and the 3-axis chosen tangent to that circle, by using (16) it is easy to see that the only action derivatives involving the 3-axis are

$$\left. \frac{\partial^2 S(\mathbf{r}'', \mathbf{r}'; \beta\hbar)}{\partial r'_3 \partial r''_3} \right|_{\substack{r'' = -\mathbf{r}^0 \\ r' = \mathbf{r}}} = \left. \frac{\partial^2 S(\mathbf{r}'', \mathbf{r}'; \beta\hbar)}{\partial r'_3 \partial r''_3} \right|_{\substack{r'' = \mathbf{r} \\ r' = \mathbf{r}^0}} = -\frac{p}{\sigma}. \quad (22)$$

Using (22) in (20) gives, when \mathbf{r} is in the neighborhood of the equatorial circle,

$$\begin{aligned} G(\mathbf{r}, -\mathbf{r}^0; \beta/2) &= (p/2\pi\hbar\sigma)^{1/2} G_2(\mathbf{r}, -\mathbf{r}^0; \beta/2); \\ G(\mathbf{r}^0, \mathbf{r}; \beta/2) &= (p/2\pi\hbar\sigma)^{1/2} G_2(\mathbf{r}^0, \mathbf{r}; \beta/2), \end{aligned} \quad (23)$$

where G_2 denotes a two-dimensional Green's function in the $(\mathbf{r}^0, \mathbf{r})$ meridian plane. Using (23) in (21), approximating the volume element $d\mathbf{r}$ by $2\pi\sigma d^2\mathbf{r}$ where $d^2\mathbf{r}$ is a surface element in the meridian plane, and applying the convolution property (21) to the two-dimensional Green's functions, we obtain

$$G(\mathbf{r}^0, -\mathbf{r}^0; \beta) = (p/\hbar) G_2(\mathbf{r}^0, -\mathbf{r}^0; \beta). \quad (24)$$

The semi-classical expression (20) can now be used for the two-dimensional Green's function G_2 in (24). The exponent $\hbar^{-1} S(-\mathbf{r}^0, \mathbf{r}^0; \beta\hbar)$ can be expanded around $r^0 = \sigma$ up to the $(r^0 - \sigma)^2$ term, and the integral (14) computed in that

saddle-point approximation:

$$A = \frac{4\pi\sigma^2 p}{\hbar} \left(\det \left| - \frac{\partial^2 S(\mathbf{r}', \mathbf{r}''; \beta\hbar)}{\partial r'_\alpha \partial r''_\beta} \right|_{\substack{r' = -r'' \\ r' = r'' = \sigma}} \right)^{1/2} \\ \times \left[2\pi\hbar \left(\frac{d^2 S(-\mathbf{r}^0, \mathbf{r}^0; \beta\hbar)}{(dr^0)^2} \right)_{r^0 = \sigma} \right]^{-1/2} \exp\left(-\frac{1}{\hbar} [S(-\mathbf{r}^0, \mathbf{r}^0; \beta\hbar)]_{r^0 = \sigma}\right), \quad (25)$$

where det means now a 2×2 determinant.

The second derivatives of the action in (25) can be explicitly computed by studying elliptical orbits in the neighborhood of the half-circle of radius σ . We omit the detail. The result is

$$A = (\beta e^4 M / 3\pi\hbar^2)^{1/2} \exp\left[-\frac{3}{2}(\pi^2 \beta e^4 M / 2\hbar^2)^{1/3}\right]. \quad (26)$$

Using (26) in (8) gives

$$\frac{\beta F_{\text{ex}}}{N} = \mp \frac{\rho}{2s+1} e^c \frac{4\pi\hbar^2 \beta^2 e^2}{M\sqrt{3}} \exp\left[-\frac{3}{2}\left(\frac{\pi^2 \beta e^4 M}{2\hbar^2}\right)^{1/3}\right]. \quad (27)$$

4. Discussion

The above derivation shows that two-body exchange effects primarily arise from particles which are at a distance σ of one another, given by (17). As σ becomes small in the near-classical limit, the replacement of r_{12} by 0 in the function W of eq. (6) becomes justified*. From (27) it is seen that the two-body exchange term decreases exponentially as $\hbar \rightarrow 0$; it may be noted, however, that this decrease is less drastic than in the hard-sphere case¹⁰, where the exchange term behaves like $\exp(-\pi M d^2 / 4\beta\hbar^2)$ for spheres of diameter d .

The magnitude of the n -body exchange effects can be estimated by a generalization of the method which has been used for the two-body case. The cyclical exchange of n particles is dominated by a classical motion in which n particles are regularly spaced on a ring which is rotated around its axis by an angle $2\pi/n$. The generalization of (15) is then satisfied since particle i has a final momentum equal to the initial momentum of particle $i+1$. The radius of the ring, as determined by classical mechanics, is easily found to be

$$R = \left((n^2 \hbar^2 \beta^2 e^2 / 16\pi^2 M) \sum_{l=1}^{n-1} [\sin(l\pi/n)]^{-1} \right)^{1/3}, \quad (28)$$

and the corresponding contribution to the free energy contains a factor

$$\exp(-S/\hbar) = \exp\left[-\frac{3}{2}\left(n\pi^2 \beta e^4 M / 4\hbar^2\right)^{1/3} \left(\sum_{l=1}^{n-1} [\sin(l\pi/n)]^{-1}\right)^{2/3}\right]. \quad (29)$$

* Corrections of higher-order in \hbar can be obtained by expanding W in a Taylor series around the configuration $(0, \mathbf{r}_{12}^0, \mathbf{r}_3^0, \dots, \mathbf{r}_N^0)$ and using a Dyson expansion for $\exp(-\beta H)^6$. One finds, as a first correction to (27), a multiplicative factor $\exp(-\beta\pi\rho e^2 \sigma^2/3)$.

Therefore, the largest contribution does come from two-body exchanges. It may be noted that this result differs from the hard-sphere one since for hard spheres three-body exchanges have been found to be dominant¹¹).

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Appendix

We give here an alternative computation of the integral A defined by (14). This integral is closely related to a previously studied one¹²). Let

$$H_2 = -(\hbar^2/M)\Delta + e^2/r \quad (30)$$

by the hamiltonian for the two-body relative motion. The thermal Green's function is related to the "time independent" one by

$$\exp(-\beta H_2) = -\pi^{-1} \operatorname{Im} \int_0^\infty \exp(-\beta \hbar^2 k^2/M) [k^2 - (M/\hbar^2)H_2]^{-1} 2k \, dk \quad (31)$$

(where k is assumed to have an infinitesimal positive imaginary part). Therefore, we can use the explicit expression¹³)

$$\langle r | [k^2 - (M/\hbar^2)H_2]^{-1} | -r \rangle = -(8\pi r)^{-1} \Gamma(1 + i\nu) W_{-i\nu, 1/2}(-4ikr), \quad (32)$$

where $\nu = Me^2/2\hbar^2 k$ and W is a Whittaker function, and write

$$A = \pi^{-1} \operatorname{Im} \int_0^\infty dr r \int_0^\infty dk k \exp(-\beta \hbar^2 k^2/M) \Gamma(1 + i\nu) W_{-i\nu, 1/2}(-4ikr). \quad (33)$$

The integral representation¹⁴)

$$\Gamma(1 + i\nu) W_{-i\nu, 1/2}(-4ikr) = -4ikr \int_0^\infty \exp[4ikr(u + \frac{1}{2})] [u/(1+u)]^{i\nu} du, \quad (34)$$

after the change of variable

$$u/(1+u) = e^{-t}, \quad (35)$$

gives

$$A = \operatorname{Im}(-i/\pi) \int_0^\infty dr r^2 \int_0^\infty dk k^2 \exp(-\beta \hbar^2 k^2/M) \int_0^\infty dt [\sinh(t/2)]^{-2} \\ \times \exp[2ikr \coth(t/2) - i\nu t]. \quad (36)$$

We perform first the integration upon r :

$$A = (4\pi)^{-1} \int_0^{\infty} dk k^{-1} \exp(-\beta \hbar^2 k^2 / M) \int_0^{\infty} dt \sinh(t/2) [\cosh(t/2)]^{-3} \sin vt. \quad (37)$$

By an integration by parts which brings the integral upon t to a tabulated form¹⁴), one obtains

$$A = \frac{1}{2} (Me^2 / 2\hbar^2)^2 \int_0^{\infty} dk k^{-3} \exp(-\beta \hbar^2 k^2 / M) [\sinh(\pi Me^2 / 2\hbar^2 k)]^{-1}. \quad (38)$$

In the near-classical limit $\hbar \rightarrow 0$,

$$A \approx (Me^2 / 2\hbar^2)^2 \int_0^{\infty} dk k^{-3} \exp[-(\beta \hbar^2 k^2 / M) - (\pi Me^2 / 2\hbar^2 k)]; \quad (39)$$

eq. (26) is recovered when a saddle-point approximation is used for (39).

The opposite limiting case, \hbar fixed and $e \rightarrow 0$, can also be studied. Eq. (38) becomes, through an obvious change of variable,

$$A = (2\pi^2)^{-1} \int_0^{\infty} dx x^{-3} (\sinh x^{-1})^{-1} + (2\pi^2)^{-1} \int_0^{\infty} dx x^{-3} (\sinh x^{-1})^{-1} \{ \exp[-(\pi^2 \beta e^4 M / 4\hbar^2) x^2] - 1 \}. \quad (40)$$

In the small e limit, $\sinh x^{-1}$ can be replaced by x^{-1} in the second integral of (40):

$$A = \frac{1}{8} - (\beta M / 16\pi \hbar^2)^{1/2} e^2 + \dots \quad (41)$$

We are now in the case $\beta e^2 \ll \lambda$, and the restriction to two-body exchanges which has been made in (8) is valid only at low density ($\lambda \ll a$), which implies that $C \rightarrow 1$. Using then (41) in (8), we correctly recover the high-temperature result

$$\frac{\beta F_{\text{ex}}}{N} = \mp \frac{\rho}{2(2s+1)} \left(\frac{\pi \hbar^2 \beta}{M} \right)^{3/2} \pm \frac{\pi \rho \hbar^2 \beta^2 e^2}{(2s+1)M}. \quad (42)$$

The first term of (42) is the degeneracy correction to the ideal gas part of the free energy, the second term is the exchange correction¹⁵) to the potential part of the free energy.

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