Uniform quantized electron gas

Johan S Høye¹ and Enrique Lomba²

¹ Institutt for Fysikk, NTNU, N-7491 Trondheim, Norway
² Instituto de Química Física Rocasolano, CSIC, Calle Serrano 119, E-28026 Madrid, Spain

E-mail: johan.hoye@ntnu.no

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Abstract

In this work we study the correlation energy of the quantized electron gas of uniform density at temperature T = 0. To do so we utilize methods from classical statistical mechanics. The basis for this is the Feynman path integral for the partition function of quantized systems. With this representation the quantum mechanical problem can be interpreted as, and is equivalent to, a classical polymer problem in four dimensions where the fourth dimension is imaginary time. Thus methods, results, and properties obtained in the statistical mechanics of classical fluids can be utilized. From this viewpoint we recover the well known RPA (random phase approximation). Then to improve it we modify the RPA by requiring the corresponding correlation function to be such that electrons with equal spins cannot be on the same position. Numerical evaluations are compared with well known results of a standard parameterization of Monte Carlo correlation energies.

Keywords: electron gas, quantization, fermions, effective interaction

(Some figures may appear in colour only in the online journal)

1. Introduction

It is a pleasure for us to contribute this article to a memorial issue for Professor George Stell. We both have had an extensive scientific collaboration with him in the research field of statistical mechanics to which he was deeply devoted. For one of us (JSH) this cooperation lasted for more than 30 years since 1973. As sketched below, developments, insights, and results through those years form a basis for the present work on the quantized electron gas.

The initial common interest back in 1973 was in the γ-ordering introduced by Hemmer [1] and by Lebowitz, Stell, and Baer [2]. The γ is the inverse range of a perturbing interaction added to a reference system, e.g. a fluid consisting of hard spheres. The γ-ordering is a resummation of the well known Mayer graph expansion in classical statistical mechanics. In this way one immediately finds a leading correction to mean field theories, like the van der Waals theory of fluids; and it is not restricted to low density as the usual low density virial expansion is. However, there are problems as divergences show up in the critical region of the gas–liquid phase transition.

With this background we initiated works on the statistical mechanics of polar fluids with dipole–dipole pair interaction. This was extended to the MSA (mean spherical approximation) of fluids where solutions of the Ornstein–Zernike equation were studied [3]. The MSA was a modification of the SM (spherical model) of spin systems [4]. It turned out to correspond to the leading order of γ-ordering beyond mean field with the additional constraint that the corresponding pair correlation function should fulfill the exact core condition for hard spheres where they cannot overlap.

Further it was realized that a fluid consisting of polarizable particles with fluctuating dipole moments modeled as harmonic oscillators, could be quantized using the methods of classical statistical mechanics [5]. In this case quantization was restricted to the internal oscillatory motions of dipole moments, not including particle positions. This extension to quantum systems was based on Feynmann’s path integral formalism [6]. The path integral turns out to be equivalent to a classical polymer problem (or random walk) problem in four dimensions, the fourth dimension being imaginary time. These polymers are periodic in the fourth dimension of length \( \beta = 1/(k_B T) \) where \( k_B \) is Boltzmann’s constant and \( T \) is temperature. This classical polymer interpretation can also be used for systems consisting of fermions as well as bosons [7, 8].

By study of and work on Casimir forces between closely separated dielectric or metal plates, it was seen that these...
forces can be interpreted as induced between quantized oscillating dipolar moments of particles [9]. Forces between ‘metal’ plates filled with classical charged particles interacting with the Coulomb interaction were also considered [10]. In this connection it was noted that the quantized electromagnetic field, since it is a linear theory, can be fully eliminated to be replaced by time-dependent (radiating) dipolar interactions. With static dipolar interactions, valid for short distances, the Casimir forces are the same as induced van der Waals forces. In this respect the quantized polarizable fluid of [5] was extended to include radiating dipolar interactions, and corrections to van der Waals forces or the free energy were obtained for the fluid in bulk [11].

Standard methods to study interacting many particle systems are the Hartree–Fock theory or DFT (density functional theory) of quantum mechanics [12]. In view of the path integral formalism this can be mapped again onto a classical polymer problem [13]. In the framework of γ-ordering, free (non-interacting) fermions (or bosons) constitute the reference system (From this viewpoint it is an ideal gas of polymers tied together into coils of varying numbers of turns. For fermions an even number of turns give negative number densities [8]). In general the quantum fluid, like electrons in molecules, has a nonuniform density due to the external potential set up by the atomic nuclei and the mean field produced by the interacting electrons. This polymer problem in mean field can be solved by means of the corresponding Schrödinger equation. This serves as a mean field solution to the statistical mechanical polymer problem, an ideal polymer gas in an external mean field. Since free fermions (or bosons) are correlated, there will also be energy contributions due to the reference system correlations. This is the well known exchange energy.

However, the pair interactions induce additional effects that contribute to a correlation energy. These correlations have been difficult to handle. They are non-local in nature, and varying methods have been used to estimate the corresponding correlation energy [14]. Broad overviews are given in the articles by Burke and Becke [15]. With our statistical mechanical development we will recover the random phase approximation (RPA) for quantized many-body systems [16, 17]. Properties found from this development will be utilized in the effort to improve upon the RPA.

In Casimir theory, induced forces follow from the dielectric properties of media. These properties again are related to molecular polarizabilities. And by elimination of the electromagnetic field (in thermal equilibrium) as mentioned above, these forces follow from induced interactions between fluctuating dipole moments. But then this energy will be part of molecular energies too and should be included [13]. Thus the correlation energy can be identified with the Casimir energy, or in the electrostatic case the van der Waals energy, in bulk. (The standard Casimir problem, however, is more limited, as only the induced free energy due to the interaction between the plates is needed to obtain the force.) This again corresponds to a contribution to leading order in γ-ordering. Here it can be noted that the statistical mechanical graph structure is valid and thus also applicable for non-uniform systems, like the system of two plates of the Casimir problem. But in the general situation the numerical problems will be much more demanding. A recent review of van der Waals forces and use of vdW-DF method to account for van der Waals interactions in DFT is given by Berland et al [18].

Here we will only consider the uniform case, but properties and results found may be applicable to the general situation. On the basic microscopic level the electron gas is not a dielectric medium, but consists of charged particles interacting via the Coulomb interaction where we will limit ourselves to the electrostatic case. The theory considered and established in the following sections will be followed by numerical evaluation of explicit results which will be compared with available results from computer simulations.

In section 2 the leading order beyond mean field in γ-ordering is considered at temperature $T = 0$. It turns out that this is equivalent to the well known RPA. Explicit RPA equations for the uniform electron gas are established. As expected, when compared with simulations there are clear deviations.

In section 3, a parameterized effective interaction, which modifies the Coulomb interaction for small distances, is considered. This is inspired by properties of the direct correlation function for classical systems, which in the MSA follows the pair potential outside the hard core diameter, but is dictated by the hard core condition inside. For fermions, like electrons, particles with equal spins cannot be at the same position. This gives a condition to determine parameters that define the effective interaction.

In section 4 the Fourier transform in space and imaginary time for the correlation function of the free uniform electron gas is given. Then the correlation functions where induced correlations are present, are established.

In section 5 the equations established are extended to those of a two-component mixture of electrons with $\pm \frac{1}{2}$ spins. Such an extension is necessary to be able to take into account that pairs of equal and unequal spins will have effective interactions that must be different for short distances.

In section 6, we will explore various effective or cut Coulomb interactions to be used in the numerical investigations of this work.

In section 7 we introduce our most significant results and discuss them in the context of well known approximations for the correlation energy of the quantized electron gas. Future prospects and conclusions are presented in section 8.

2. Random phase approximation

The Fourier transform (in space) of the pair correlation function or structure factor for free bosons and fermions is given by [8, 19]

$$\tilde{S}(\lambda, k) = \frac{\zeta}{(2\pi)^3} \int \frac{\bar{F}_\lambda(k')\bar{F}_{\lambda-\lambda}(k'')}{(1 \pm \chi)(1 \pm \chi') \pm i} dk'$$

(1)

where $k'' = k - k'$ and $\lambda = \pi t/h$ ($t$ is time), $0 < \lambda < \beta$. The $\beta = 1/(k_B T)$ where $k_B$ is Boltzmann’s constant and $T$ is temperature. Further

$$F_\lambda(k) = \exp(-\lambda E(k)), \quad \chi = F_\beta(k'), \quad \text{and} \quad Y = F_\beta(k'')$$

(2)
where \(E(k)\) is the energy of particles with mass \(m\), i.e.
\[
E(k) = \frac{1}{2m}(hk)^2.  
\]

Finally \(\zeta = e^{i\mu}\) where \(\mu\) is the chemical potential. In equation (1) the plus sign is for fermions while the minus sign is for bosons. By Fourier transform in imaginary time \(\hat{S}(K,k) = \int_0^\beta \hat{S}(\lambda,k)e^{iK\lambda}d\lambda\) one obtains
\[
\hat{S}(K,k) = \frac{\zeta}{(2\pi)^3} \int \frac{1}{iK + \Delta(1 \pm iX)(1 \pm iY)}dk'.
\]

where \(\Delta = E(k') - E(k)\) and \(K = 2\pi n/\beta\) with \(n\) integer are the Matsubara frequencies.

Now the charged particles (electrons) interact via the Coulomb interaction \(\psi(r) = e^2/(4\pi\varepsilon_0 r)\) (in SI units) whose Fourier transform is
\[
\tilde{\psi}(k) = \frac{e^2}{\varepsilon_0 k^2}.
\]
The \(-e\) is the electron charge while \(\varepsilon_0\) is the permittivity of vacuum.

The non-interacting particles form the reference system electron gas of fermions. To obtain the contribution to the free energy from the pair interaction we follow the \(\gamma\)-ordering scheme developed for classical fluids [1, 2]. The \(\gamma\) is the perturbing parameter, and it is the inverse range of attraction (For Coulomb interaction the \(\gamma\) may be regarded as the inverse range of the shielded Coulomb interaction that follows from summation of chain bond graphs that also lead to the well known Debye–Hückel theory).

The leading contribution to Helmholtz free energy \(\Delta F\) now follows from summation of the ring graphs with potential bonds and is given by [20]
\[
-\beta \Delta F = -\frac{1}{2(2\pi)^3} \sum_k \int dk \ln[1 - g\hat{S}(K,k)(-\tilde{\psi}(k))]  
\]
where \(g = 2\) takes into account degeneracy of up and down electron spins (that for free electrons are uncorrelated).

By expansion of the logarithm the linear term can be separated out as
\[
-\beta \Delta F_{\text{ex}} = -\frac{g^2\beta}{2(2\pi)^3} \int \int dk \hat{S}(K,k)(-\tilde{\psi}(k))  
\]

since \((1/\beta) \sum_k \hat{S}(K,k) = \hat{S}(0,k)\) (i.e. \(\lambda = 0\)). The \(\Delta F_{\text{ex}}\) is the well known exchange energy. Remaining free energy is the non-local part, the correlation energy, due to induced correlations from the pair interactions. We are interested in the ground state energy at \(T = 0\) by which \(\beta \to \infty\), and \((1/\beta) \sum_k \to (1/(2\pi)) \int dK\). At \(T = 0\) entropy is zero for quantum systems by which internal energy is the same as Helmholtz free energy. Thus the correlation energy per unit volume becomes
\[
-\Delta F_c = -\frac{1}{2(2\pi)^3} \frac{1}{2\pi} \int dK \int dK' \int \int [\ln(1 - \hat{A}(K)) - \hat{A}(K)],
\]

This expression for \(\Delta F_c\) turns out to be the same as the RPA (random phase approximation) [16, 17].

With known \(\hat{S}(K,k)\) equation (8) can be integrated numerically. In [20] a very crude approximation \(\hat{S}(K,k) = 2\Delta \hat{S}(0,k)(K' + \Delta')\) (with \(\Delta \sim k\)) was used to enable analytic integration with respect to \(K\) to perform further analysis. However, integral (4) for \(\hat{S}(K,k)\) can be evaluated analytically for \(T = 0\). The result is given by the Lindhard function \(\chi_0\), equation (28) of [17], which in our notation below is
\[
g\hat{S}(K,k) = -\chi_0 = \frac{m\varepsilon_0 k}{2\pi^2 h^2} f(Q,x)  
\]

\[
f(Q,x) = -\left[\frac{Q^2 - x^2 - 1}{4Q} \ln \left(\frac{x^2 + (Q + 1)^2}{x^2 + (Q - 1)^2}\right)\right]  
\]

\[
-1 + x \arctan \left(\frac{1 + Q}{x}\right) + x \arctan \left(\frac{1 - Q}{x}\right)  
\]

with \(x = mK/\hbar^2k_i = K/4\mu Q\), \(\mu = (h/k)^2 = Q/k = 2k_i\)

where \(\mu\) is the Fermi energy and \(k_i\) is the Fermi wave vector.

With this and interaction (5) the quantity \(\hat{A}(K)\) in expression (8) for the energy can be expressed as
\[
\hat{A}(K) = D f(Q,x)  
\]

\[
D = \frac{mk_i}{2\pi^2 h^2 \varepsilon_0 (2k)^2} = \frac{3}{32} \left(\frac{h}{\mu}\right)^2  
\]

The \(\omega_p\) is the plasma frequency
\[
\omega_p^2 = \frac{\rho e^2}{m\varepsilon_0}  
\]

where \(\rho\) is the number density of particles given by \(T \to 0\) [20]

\[
\rho = \frac{g}{(2\pi)^3} \int \frac{dX}{1 + \chi} \int \frac{dk}{2\pi} = \frac{4\pi g}{3(2\pi)^3} k_i^3.  
\]

For the quantized electron gas at \(T = 0\) there is only one independent parameter. A standard choice is the parameter \(r_1\) given by
\[
\frac{4\pi}{3} (ra_0)^3 = \frac{1}{\rho}, \quad a_0 = \frac{4\pi \varepsilon_0 \hbar^2}{me^2}  
\]

where \(a_0\) is the Bohr radius. With this definition, \(r_1\) is unitless. Inserting for \(a_0\) and \(\rho\) one finds
\[
r_1 = 12.0584 \cdot D \quad \text{or} \quad D = 0.0829239 \cdot r_1  
\]

with \(D\) given by equation (13). For the correlation energy per particle equation (8) can be rewritten as
\[
\frac{f_c}{\rho} = 12 \int_0^\infty f_c(k)Q^2 dQ  
\]
with \( \rho \) given by equation (15) and \( x, \mu, \) and \( Q \) given by equation (12). Since \( \mu \sim k_t^2 \) and \( r_t \sim \rho^{1/3} \sim k_t^{-1} \) it follows that

\[
\mu = \mu(r_t) = \frac{\mu(r_t = 1)}{r_t^2} = \frac{50.1 \text{ eV}}{r_t^2}
\]  

(20)

with \( \hbar = 1.054 \times 10^{-34} \text{ J} \cdot \text{s} \) and electron mass \( m = 9.11 \times 10^{-31} \text{ kg} \).

In figure 2 of [17] results for the distribution of energies \((Q = k_h(2k_t))\)

\[
e_{\rho}(Q) = 12\rho_c(k)Q^2
\]

(21)

are plotted as function as function of \( Q \) for \( r_t = 4 \). There one of the curves is the one of the RPA which is reproduced by the expressions established above. These expressions will be a basis for the modifications performed below to improve results.

3. Effective interaction

For classical fluids various properties or conditions can be utilized to improve results. One such condition is the hard sphere condition which we will focus upon here. This implies that particles can not overlap within their hard core radii. This is expressed through the pair correlation function \( h(r) \) that can be required to have its exact value \(-1\) (with standard definition of \( h(r) \)) within the hard core diameter. But the main problem is that the hard core influences the correlation function in a highly non-trivial way outside the hard core. The latter problem, however, is resolved by considering the direct correlation function \( c(r) \) where simple approximations can be made [21]. The \( h(r) \) and \( c(r) \) for classical fluids are related to each other via the Ornstein–Zernike integral equation which is similar to the Dyson type equation (25) below (with its \( \bar{S}(K, k) \) replaced with \( \rho \)).

It is known that to a leading approximation the \( c(r) \) is \(-\beta \psi(r) \) where \( \psi(r) \) is the perturbing interaction. Further this becomes exact for large \( r \to \infty \). For small \( r \) there will be deviations. In the MSA (mean spherical approximation) these deviations are defined to be inside the range of the hard core diameter. With this and the hard core condition on \( h(r) \) as boundary conditions the resulting \( h(r) \) can be determined for all \( r \). With known \( h(r) \) the equation of state can be obtained both via the internal energy route and the compressibility route. Since MSA is not exact these routes give different results, a measure of resulting inaccuracy.

Then the SCOZA (self-consistent Ornstein–Zernike approximation) was introduced where the MSA was used with \( \beta \) replaced by an effective inverse temperature \( \beta_\varepsilon \) requiring both routes to thermodynamics to give the same result [22]. This resulted in a non-linear partial differential equation. By numerical solution of this equation very accurate results came out, also in the ‘non-classical’ critical region [23, 24]. A related fluid theory, the HRT (hierarchical reference theory), based upon the renormalization group approach also gives very accurate results [25]. The critical indices of the latter have by analytic and numerical work been found to be simple numbers [26]. It is not ruled out that these indices are the exact ones for fluids, lattice gases, and spin systems in three dimensions. Anyway, it is thus demonstrated that the exact \( c(r) \) deviates from its MSA form by some function the form of which is not crucial for accurate results.

Further the MSA was extended to polymers where the reference system was hard spheres tied together into polymer chains [27]. Again the MSA type \( c(r) \) gave reasonably good results. These properties are expected to carry over to the ‘polymer’ path integral of quantized systems. Then in the RPA the \( \psi(r) \) plays the role of the \( c(r) \). Again this should be exact as \( r \to \infty \) while for small \( r \) there will be modifications that will replace \( \psi(r) \).

The latter polymer problem in 3 dimensions is similar to the polymer or random walk like path integral of quantum mechanics in 4 dimensions. In the RPA the interaction \( \psi(r) \) plays the role of the \( c(r) \). Again this should be exact as \( r \to \infty \) while for small \( r \) there will be modifications. Thus similar to classical fluids this will replace the \( \psi(r) \) with an effective interaction. Similar efforts have been done earlier [17]. A key problem in this context has been how to specify the effective interaction more precisely.

Thanks to the above connection to classical fluids, we can impose similar conditions to the path integral ‘polymers’ of quantized electrons that interact. Electrons are fermions that behave as hard spheres in the sense that they are not allowed to occupy the same site if their spins are equal. Thus one can apply a hard sphere condition on the equal time pair correlation function for electrons with equal spins at the same position. For slightly different positions the situation is less clear as electrons start to overlap. However, one will expect that the effective interaction must transform to the \( \psi(r) \) in a smooth way during a distance corresponding to the one between particles or the inverse of the Fermi wave vector \( k_t \) as \( r \) increases. Due to the repulsive Coulomb interaction one might expect the same hard core condition for unequal spins. We will find, however, that the latter fails especially when the parameter \( r_t \) decreases. The reason is apparently that quantum mechanically the wave function does not go down to zero at \( r = 0 \) with repulsive Coulomb interaction between unequal spins. Due to increasing fermion pressure with density, this overlap will increase with decreasing \( r_t \).

4. Correlation function and core condition

The structure function of the free Fermi gas is given by equation (4) together with explicit expressions (10) and (12). The equal time pair correlation function \( h_\delta(r) \) \((i = 1, 2 \text{ for } \pm \frac{1}{2} \text{ spins}) \) is related to it as (at \( T = 0 \))
\[ S(0, r) = \rho \delta(r) + \hat{\rho}^2 h_d(r), \quad \rho_1 = \frac{\rho}{2}. \]  

(22)

Explicitly one has
\[ h_d(r) = -(g(r))^2, \quad g(r) = \frac{3(\sin \gamma - \gamma \cos \gamma)}{\gamma^3}, \quad \gamma = k(r). \]  

(23)

As \( g(r) \to 1 \) when \( r \to 0 \), the fermion condition \( h_d(0) = -1 \) is fulfilled. For unequal uncorrelated spins \( h_d(0) = -1 \). Further for the equal time Fourier transform \((g = 2)\)
\[ g\hat{S}(0, k) = \begin{cases} \rho(\frac{3}{2}Q - \frac{1}{2}Q^2), & Q < 1 \\ \rho, & Q > 1 \end{cases} \]  

(24)

with \( Q \) and \( \rho \) given by equations \((12)\) and \((15)\).

By \( \gamma \)-ordering the leading correction to the reference system pair correlation function are the graphs that form the chain bond expression. This also coincides with the RPA and is given by \([17]\)
\[ g\hat{\Gamma}(K, k) = \frac{g\hat{S}(K, k)}{1 + \hat{A}(K)} \]  

(25)

with \( \hat{A}(K) \) given by equation \((13)\). Here, so far, the electron gas is considered as a one-component fluid by which an average of correlations between equal and unequal spins is obtained.

Now we can introduce the effective interaction where the Coulomb interaction is modified for small \( r \). We will also keep it finite for small \( r \to 0 \) although this may not be required since singular behavior will be smoothed out with equation \((25)\). In \( k \)-space the modification is equivalent to a smooth cut for large \( k \). Thus the interaction \((5)\) is replaced by an effective interaction
\[ \psi_k(k) = \hat{\psi}(k) \hat{L}(Q), \quad \hat{L}(0) = 1. \]  

(26)

In \( r \)-space, where it turned out more convenient to find a suitable functional form, this can be written
\[ \psi_k(r) = \psi(r) \hat{f}(r), \quad \hat{f}(r) \to 1 \quad \text{as} \quad r \to \infty. \]  

(27)

The \( f(r) \) will contain a free parameter that may be determined by a core condition at \( r = 0 \).

With the crude analytic evaluations made in \([20]\) it was noted that the ‘exact’ energy distribution could be reproduced rather well by a suitable choice of \( \hat{L}(Q) \) after first modifying the crude approximation for \( \hat{S}(K, k) \) (as given in text above equation \((10)\)) to fit the RPA of figure 2 in \([17]\).

Here we want to use the core condition to see to which extent ‘exact’ results from computer simulations can be recovered when implementing it. With equation \((25)\) one can impose an average hard core condition for equal and unequal spins. From equations \((22)\) and \((23)\) follows as \( r \to 0 \)
\[ g\hat{S}(0, r) = \rho \delta(r) - \frac{1}{2} \rho^2. \]  

(28)

This is 1/2 of a hard core condition for both equal and unequal spins taken together. So a corresponding full hard core condition on the average requires \((g = 2)\)
\[ \Gamma(0, 0) - S(0, 0) = -\frac{1}{4} \rho^2. \]  

(29)

The resulting energy distribution \((21)\) has been evaluated numerically using various forms of the function \( f(r) \) that cuts the potential. In order to evaluate \((29)\) one considers
\[ \Delta \hat{\Gamma}(K, k) = \hat{\Gamma}(K, k) - \hat{S}(K, k), \]  

(30)

and integrate to find
\[ \Delta \Gamma(0, k) = \frac{1}{2\pi} \int \Delta \hat{\Gamma}(K, k) dK = \frac{4\mu Q}{2\pi} \int_{-\infty}^{\infty} \Delta \hat{\Gamma}(K, k) dx, \]  

(31)

with use of equations \((10)\) and \((12)\). Further
\[ \Delta \Gamma(0, 0) = \frac{1}{(2\pi)^3} \int \Delta \hat{\Gamma}(0, k) dk = 2\left(\frac{\rho}{2}\right) \int_{0}^{\infty} \Delta \hat{\Gamma}(0, 0) Q^2 dQ. \]  

(32)

where also equation \((15)\) is used. This together with condition \((29)\) will determine a free parameter in the effective potential \((27)\).

We have tried some different forms for the cut function \( f(r) \) and considered the case \( r_1 = 4 \) where results are available in \([17]\) in the form of the Perdew–Wang parameterization \([29]\) of Monte Carlo results \([30]\). By use of the average core condition \((29)\) the results obtained are seen in figure 1 for various effective cut interactions (see section 6 below). As seen from the figure results obtained were near the exact curve, considerably improving upon the RPA curve, but with some deviations especially for large \( Q \).

However, in this calculation we have not taken into account that equal and unequal pairs of spins correlate differently. This means that effective interactions have to be different to fulfill the core conditions in more detail, especially the one for equal spins that is strict. Moreover, it turned out, as mentioned earlier, that the strict core condition could not be maintained for all electron densities and \( k \)-values on unequal pairs of spins. This condition had to be abandoned as computations finally would no longer converge for increasing density. Study of the Schrödinger equation shows that the repulsive Coulomb potential can not prevent overlap of unequal particles. Due to increasing fermion pressure this overlap increases for higher density.

### 5. Mixture of electrons with ±1/2 spins

With a mixture of \(+\frac{1}{2}\) spins the correlation function will be a 2 × 2 matrix. To simplify we introduce the matrices
\[ M_+ = \frac{1}{2} \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}, \quad M_- = \frac{1}{2} \begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix}. \]  

(33)

\[ M^2 = M_+ + M_-, \quad M_+ M_- = 0. \]

The reference system correlation function can now be written as
\[ \hat{S}(K, k) \to \hat{S}(K, k)(M_+ + M_-). \]  

(34)

Likewise the Coulomb interaction can be written as
However, the effective or cut interaction will be different for equal and unequal pairs of spins

\[ \tilde{\psi}(k) \rightarrow 2\tilde{\psi}(k)M_+ + \tilde{\psi}(k)M_- \]  

Finally the resulting correlation function becomes

\[ \hat{\Gamma}(K, k) \rightarrow \hat{\Gamma}_+ (K, k)M_+ + \hat{\Gamma}_-(K, k)M_- \]  

with

\[ \hat{\Gamma}_\pm (K, k) = \frac{\hat{S}(K, k)}{1 \pm \hat{A}_\pm (K)} \]  

\[ \hat{A}_\pm (K) = -g\hat{S}(K, k)(-\tilde{\psi}_\pm (k)) = D \frac{f(Q, x)}{Q^2} L_\pm (Q) \]  

The latter expression is a generalization of equations (8), (13) and (26) when properties (33) for the matrix multiplications are used. With the free energy per particle (19) is modified to

\[ f_\xi (k) = \frac{1}{\pi} \frac{\mu Q}{2} \left\{ \int [\ln (1 + \hat{A}_+(K)) - \hat{A}_+(K)] \, dx + \int [\ln (1 + \hat{A}_-(K)) - \hat{A}_-(K)] \, dx \right\} \]  

This is used in the energy distribution \( \varepsilon_\xi (Q) \) given by equation (21) as before. Expression (40) for the free energy assumes that it keeps its MSA form also with effective interaction as is the case with classical hard spheres. However, from some of the various approximations considered in [17], we realize that this may be modified. But in the present investigation this will not be considered.

Like equations (30)–(32) one now has

\[ \Delta \hat{\Gamma}_\pm (K, k) = \hat{\Gamma}_\pm (K, k) - \hat{S}(K, k) \]  

\[ \Delta \hat{\Gamma}_\pm (0, k) = \frac{4\mu Q}{2\pi} \left[ \int_{-\infty}^{\infty} \Delta \hat{\Gamma}_\pm (K, k) \, dx \right] \]  

\[ \Delta \Gamma_\pm (0, 0) = 24 \left( \frac{\rho}{2} \right) \int_{0}^{\infty} \Delta \hat{\Gamma}_\pm (0, k)Q^2 \, dQ \]  

With expressions (10), (12), and (15) for \( g\hat{S}(K, k), \mu, \) and \( \rho \) respectively equation (38) gives (\( g = 2 \))

\[ 4\mu Q \frac{\hat{S}(K, k)}{2\pi} = \frac{3Q}{2\pi} \left( \frac{\rho}{2} \right) \frac{f(Q, x)}{1 + A_\pm (K)} \]  

by which

\[ \Delta \Gamma_\pm (0, 0) = - \frac{36}{\pi} \left( \frac{\rho}{2} \right)^2 \int_{0}^{\infty} \int_{0}^{\infty} \frac{f(Q, x)A_\pm (K)}{1 + A_\pm (K)} \, dx \, dQ \]  

With a strict core condition also on unequal spins the core condition like equation (29) would be modified into

\[ \Delta \Gamma_\pm (0, 0) = \mp \frac{1}{4} \frac{\rho^2}{r^2} \]  

With this equation (37) for the mixture correlation function together with equation (28) for \( S(0, 0) \) would give (\( r \rightarrow 0, \rho_0 = \rho/2 \))

\[ \Gamma_\xi (0, 0)M_+ + \Gamma_\xi (0, 0)M_- = \frac{\rho}{2} \hat{S}(r) - \left( \frac{\rho}{2} \right)^2 \left[ \begin{array}{cc} 1 & 1 \\ 1 & 1 \end{array} \right] \]  

However, it turned out that in a quantum mechanical framework the strict hard core condition on unequal spins was not valid as mentioned at the end of the previous section, and the solution of (44) can not be found for high density. This implies that equation (44) has to be abandoned to be replaced by (\( a < \rho^2/4 \))

\[ \Delta \Gamma_\pm (0, 0) = \mp a \quad \text{or} \quad \Delta \Gamma_\xi (0, 0) + \Delta \Gamma_\xi (0, 0) = 0 \]
6. Cut interaction

As mentioned before, the interaction is to be cut in a smooth way and will contain one or more parameters to be determined in terms of the core condition. In this work we have the exact condition (46), and two free parameters are needed. This means that some freedom remains, in addition to the form of the functions used. In particular, the functions considered in this investigation were of the form

\[ \psi_s(r) = \psi(r)f(r), \quad \psi(r) = \frac{1}{4\pi r_0^2} \]

with \( f(r) \) equal to a sharp cutoff, a simple exponential, a smoothed exponential (with zero slope at the origin), an error function and a smooth Gaussian function (whose value and derivative vanish as \( r \to 0 \)), i.e.

\[ H(x-1), \quad 1 - e^{-x^2}, \quad 1 - (1 + x/2)e^{-x^2}, \quad \text{erf}(x), \quad \text{and} \quad 1 - (1 + x^2)e^{-x^2} \]

respectively. Here \( x = 2k_Hr \), where \( k \) is a free parameter \( (H(x-1) \text{ is a Heaviside function, and } \text{erf}(x) = (2/\sqrt{\pi}) \times \int_0^x \exp(-u^2) \text{d}u) \). The corresponding Fourier transforms are given by \( \psi_s(k) = (1/(\kappa^2k^2))L_+(Q) \) with \( L_+(Q) \) equal to

\[ L_{\text{sharp}}(Q) = \cos(Q/\kappa) \]

\[ L_{\text{exp}}(Q) = \frac{\kappa^2}{Q^2 + \kappa^2}, \]

\[ L_{\text{exp}}(Q) = \left( \frac{\kappa^2}{Q^2 + \kappa^2} \right)^2, \]

\[ L_{\text{exp}}(Q) = \exp(-Q^2/(2\kappa)^2), \]

\[ L_{\text{exp}}(Q) = 1 - Q^2 \left( \frac{3}{2} \frac{Q^2}{4\kappa^2} \frac{D_s(Q^2/2\kappa)}{\kappa^2} + \frac{1}{4\kappa^2} \right) \] (53)

respectively, with \( D_s(x) \) being Dawson’s integral [28], i.e.

\[ D_s(x) = \frac{1}{2} \int_0^\infty e^{-u^2/4} \sin(ux) \text{d}u = e^{-x^2} \int_0^\infty e^t \text{d}t. \] (54)

The last equality follows as both expressions solve the differential equation \( y' + 2xy = 1 \). A graphical representation of the various cut interactions in Fourier space can be seen in figure 2.

We also have to specify \( \psi_s(r) \), which is a function of short range. With \( \psi_s(r) = \psi(r)L_+(Q) \) the choice

\[ L_+(Q) = -\tau Q^2 L_+(Q) \] (55)

with one additional free parameter \( \tau \) was made. Effectively this means that the previous Coulomb interaction of \( \psi_s(r) \) is replaced with a shielded one \((1/Q^2 \to L_+(Q))\). This is of course a crude approximation, but \( \psi_s(r) \) is less significant than \( \psi_s(r) \), since the former only deals with the difference between particle pairs of either equal or unequal spins.

7. Numerical results

At the end of section 4, figure 1 was found by using the average hard core condition (29). Further it was remarked that after further considerations the strict hard core condition would not be valid for unequal spins. Likewise the corresponding strict condition (44) should be replaced by condition (46) with a free parameter \( a \leq (\rho/2)^2 \). So for further computations in this work we chose to use

\[ \Delta \Gamma_\pm(0,0) = \pm \frac{1}{2} \left( \frac{\rho}{2} \right)^2. \] (56)

With this and expression (39) for \( A_\pm(K) \) the core condition for \( \Delta \Gamma_\pm(0,0) \) can be cast into \((L_+(Q,\kappa) = L_+(Q), L_-(Q,\kappa,\tau) = L_-(Q))\).
The above integrals have been evaluated up to \( k = 16k_F \) (i.e. \( Q = 8 \)) with 2000 points and \( x = 10 \) with 1000 points. For \( r_s = 4 \) solution of the core conditions yields \( \kappa = 1.241 \) and \( \tau = 0.617 \). With this we have obtained the results shown in figure 3. Here one first can note the good accuracy with which the Gaussian cut reproduces the ‘exact’ correlation energy distribution. However, a second feature to be pointed out in this figure is the breakdown of the results of our approximation when the effective cut potential used corresponds to the simple exponential cut, (50), the smooth exponential, (51), and the error function, (52), as \( \kappa \) decreases. This breakdown occurs in the \( \Delta \Gamma \) part of the core condition (46). By a closer study of numerical results we found the breakdown connected to the denominator of equation (58) which became zero (as \( L_+(Q) < 0 \)). Thus the chosen core condition (56) could no longer be fulfilled for these functions. By making the core condition parameter \( a \) of equation (46) smaller the breakdown may be prevented. But the main problem here may be connected to the crude guess for the function form (55) chosen. Anyway, we did not pursue this problem further in this work. Instead we investigated more closely the two other cut potentials.

Interestingly, when the cut interactions vanish as \( r \to 0 \)—as is the case of the sharp cut, (49), and the Gaussian cut, (53)—the core condition can be solved. One observes that the Gaussian cut reproduces accurately the ‘exact’ results obtained from the Perdew–Wang parameterization of the correlation energy [17, 29], with small (around one percent) deviations close to the minimum at \( k = 0.57k_F \). In what follows, we will restrict our discussion to the results obtained with the Gaussian cut effective interaction.

We can now proceed to calculate the full correlation energy as

\[
E_c(r_s) = \int \varepsilon_c(Q)dQ
\]
that would only require the solution of the core conditions for moderate electron densities.

Now, we can compare our results with those of other approximations in figure 5. The approximations included in the figure are the adiabatic local density approximation [17] (ALDA), the RPA, the parameterization of Corradini et al [31], the approximation of Petersilka, Grossman and Gross [32] (PGG) and the local approximation of Richards and Ashcroft [33] (LRA). The full approximation of Richards and Ashcroft [33] (RA) practically coincides with the PW parameterization and it is not included. With the exception of the full RA approximation, we observe that our approximation with the two parameters fixed for \( r_s < 4 \) clearly outperforms all other approximations, exhibiting appreciable differences only at very high electron densities.

8. Conclusion

We have studied the correlation energy of the quantized electron gas at uniform density. In view of the path integral the well known RPA was recovered. The RPA can be interpreted in terms of a classical statistical mechanical polymer problem in four dimensions. Methods and reasoning of classical systems are thus utilized by which the Coulomb interaction is modified for short distances to be replaced by an effective one. Then, as imposed via the pair correlation function, particle pairs of equal spins are not allowed to be at the same position. We have found numerical results in excellent agreement with well established parameterizations like the one proposed by Perdew and Wang [29]. However, this required some extra adjustments of coefficients as described in the previous

Figure 4. Integrated electron correlation energy computed for the Gaussian cut effective interaction (equation (53)). The cases studied are the one with core condition (56) (i.e. equations (57) and (58) are fulfilled), then \( \kappa \) is kept constant (i.e. only equation (58) is solved), and finally both \( \kappa \) and \( \tau \) are kept constant. The constant values of \( \kappa \) and \( \tau \) are determined solving for the core conditions at \( r_s = 4 \). The reference values, fully drawn curve, are those of the Perdew–Wang parameterization [29].

Figure 5. Deviation of the electron correlation energy computed using the approximated core conditions in this work and using other approximations from the literature (see the text for definitions) with respect to the Perdew–Wang parameterization [29].
section. So in view of this and the remark below equation (40) further investigations are needed to possibly better straighten out problems that appeared or make other improvements. We expect that results obtained for the effective interaction for various electron densities may be extended to and utilized for the non-uniform electron gas in molecules and on periodic lattices to possibly obtain more accurate correlation energies.

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