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On the Coulomb Energy of a Finite-Temperature Electron Gas

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We rederive the Coulomb expansion of the electron gas average energy at finite temperature, starting from scratch, i.e., using only the framework of the grand canonical ensemble and not the finite-T Green's function formalism. We recover the analytical expressions of the exchange and correlation energy in both the high-T and the $T=0$ limits. We explicitly show the origin of the crossover of the correlation energy leading term from $e^4 \ln e^2$ at zero temperature to e^3 at finite T. We also discuss the relative importance of exchange and correlation in both limits.

KEY WORDS: Finite-T electron gas; Coulomb expansion of the thermodynamic potential; degenerate/nondegenerate limits; exchange and correlation energies.

1. INTRODUCTION

Many-body effects resulting from Coulomb interaction between carriers have aroused considerable interest for a long time. They were first studied in metals, in which the electron gas is always degenerate. In semiconductors, the carrier density can be varied either by doping or by laser irradiation, so that many-body effects can be studied from the nondegenerate to the quantum limit.

At $T=0$, differents methods$^{(1-5)}$ have been proposed to calculate the Coulomb energy. They all rely on a Coulomb perturbative expansion valid when the interparticle distance is much smaller than the Bohr radius (except the Monte Carlo calculation developed by Ceperley$^{(5)}$). This

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perturbative treatment has been greatly simplified by the introduction of the Green's function formalism.(2-4) At finite temperature, the Coulomb energy has also been obtained from this formalism, using Matsubara's method.(3,6-11) Although quite visual, this formalism contains many simplifying rules which hide some important aspects of the problem. This is why we find it instructive and useful to rederive the finite-temperature Coulomb energy from scratch, with statistical mechanics only, following step by step the elimination of the various irrelevant terms.

The appropriate procedure to calculate the Coulomb energy of an N-electron gas in thermal equilibrium is to work in a grand canonical ensemble defined by a temperature T and a chemical potential μ. From the grand partition function Ξ, calculated as an expansion in the Coulomb interaction, we derive the thermodynamic potential Ω, the average energy $\bar{E}$, and particle number $\bar{N}$. By imposing $\bar{N}=N$, we find the appropriate μ. We then calculate the exchange and correlation energies in the high-T limit, i.e., when the thermal length is much smaller than both the interparticle distance and the Bohr radius. We also rederive the well-known $T=0$ energy from the same approach. This allows us to identify clearly the origin of the difference between the e^3 behavior of the correlation leading term at finite temperature and the $e^4 \ln e^2$ behavior at $T=0$.

The paper is organized as follows: in Section 2 we give some qualitative arguments which help to understand the density and temperature dependences of the Coulomb energy; in Section 3 we establish the formalism and derive the Coulomb expansion of the thermodynamic potential at finite T; in Section 4 we calculate the Coulomb energy in the high-T limit; in Section 5 we recover the $T=0$ Coulomb energy using the same approach. We also obtain the small-T behavior of the correlation energy.

2. QUALITATIVE DISCUSSION

The Coulomb energy of N electrons in a volume v at the temperature T is controlled by three characteristic lengths:

(i) The average distance between electrons d defined by

$$4\pi d^3/3 = v/N = 1/n \tag{2.1}$$

(ii) The thermal length λ_T defined by

$$\pi k_B T = \hbar^2(2\pi/\lambda_T)^2/2m \tag{2.2}$$

(iii) The Bohr radius a_0, which is the length associated with the Coulomb interaction

$$a_0 = \hbar^2\varepsilon_0/me^2 \tag{2.3}$$

The relative values of d, λ_T, and r_s determine various regimes for which different approaches to the Coulomb energy calculation can be proposed (see Fig. 1).

In the $T=0$ *limit*, there is only one dimensionless parameter

$$r_s = d/a_0 \tag{2.4}$$

As r_s is proportional to e^2, a Coulomb expansion of the energy appears as a small-r_s expansion, $\tilde{\varepsilon}(T=0)=\mu_F(\alpha_0+\alpha_1 r_s+\alpha_2 r_s^2+\cdots)$, where μ_F is the Fermi energy

$$\mu_F = \hbar^2 K_F^2/2m = (9\pi/4)^{2/3} R_0/r_s^2 \tag{2.5}$$

$R_0 = me^4/2\hbar^2\varepsilon_0^2$ is the Rydberg energy. However, in three dimensions the quadratic term as well as all higher-order terms diverge, due to the long-range character of the Coulomb interaction. The summation of these singular terms gives rise to a screening of the interaction characterized by a q_s wavevector

$$q_s^2 = (4\pi e^2/\varepsilon_0)\, \partial n/\partial\mu \tag{2.6}$$

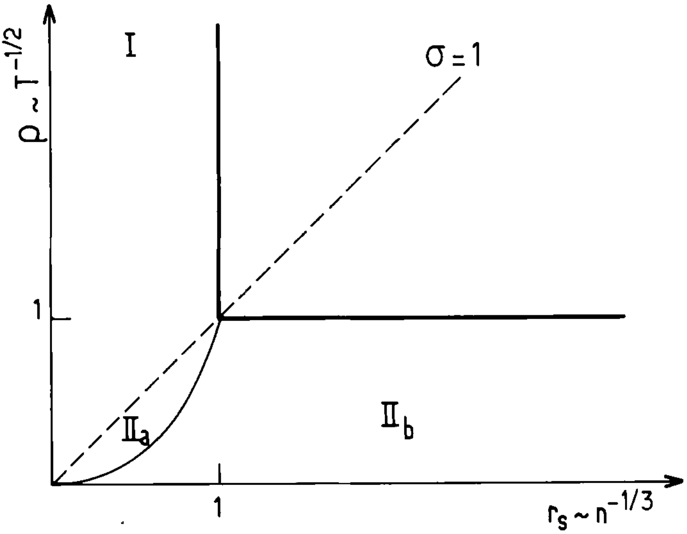

Fig. 1. Domains of validity of the small-r_s expansion in the $T=0$ limit (I) and small-ρ expansion in the high-T Boltzmann limit (II). In I and II$_a$ the exchange energy is larger than the correlation energy, while in II$_b$ the correlation energy is the largest. ρ and r_s are, respectively, the thermal length and interparticle distance in units of the Bohr radius.

in which μ has to be replaced by its $T=0$ value, μ_F. The corresponding contribution turns out to be proportional to $r_s^2 \ln r_s$ (i.e., to $e^4 \ln e^2$) instead of r_s^2. The $T=0$ Coulomb energy thus reads

$$\bar{\varepsilon}_{\text{Coul}}(T=0) = R_0[\alpha_1' r_s^{-1} + \alpha_2' \ln r_s + \alpha_2'' + O(r_s)] \tag{2.7}$$

This small-r_s expansion is valid for small average distance d, i.e., large electron density (domain I of Fig. 1). For small density, i.e., large r_s, the electrons form a Wigner crystal instead of an electron gas, the Coulomb interaction being dominant in this limit.

At finite temperature, two other dimensionless parameters can be built up from the three characteristic lengths,

$$\rho = \lambda_T/a_0 = (4\pi R_0/k_B T)^{1/2} \tag{2.8}$$

which is proportional to e^2, and

$$\sigma = \lambda_T/d = \rho/r_s = (4/9\pi)^{1/3}(4\pi\mu_F/k_B T)^{1/2} \tag{2.9}$$

which is independent of e^2. The parameter σ differentiates the quantum (degenerate) limit from the Boltzmann (nondegenerate) limit, which correspond to $\sigma \gg 1$ and $\sigma \ll 1$, respectively. At finite T, the energy depends on two of these three parameters r_s, ρ, and σ.

Since in the high-T Boltzmann limit ($\rho \ll 1$, $\sigma \ll 1$, i.e., domain II of Fig. 1) the kinetic part of the energy is not proportional to μ_F but to $k_B T$, the expansion parameter, proportional to e^2, is no longer r_s but ρ. We now expect an e^2 expansion like $\bar{\varepsilon}(T) = k_B T[3/2 + \beta_1(\sigma)\rho + \beta_2(\sigma)\rho^2 + \cdots]$. Here again the quadratic term diverges; the summation of the singular terms screens out the Coulomb potential, the screening wavevector being still given by Eq. (2.6), in which μ has to be replaced by its classical expression

$$\mu_T = k_B T \ln(n\lambda_T^3/2) \equiv k_B T \ln(3\sigma^3/8\pi) \tag{2.10}$$

Since the singularity of the quadratic term is in fact larger at high T than at $T=0$, the resulting contribution is in $\rho^2 \rho^{-1/2}$ (i.e., e^3) instead of $r_s^2 \ln r_s$ (i.e., $e^4 \ln e^2$). The average energy eventually reads

$$\bar{\varepsilon}(T) = k_B T[3/2 + \beta_1(\sigma)\rho + \beta_2'(\sigma)\,\rho^{3/2} + \cdots] \tag{2.11}$$

The T and n dependences of $\bar{\varepsilon}(T)$ depend on the σ dependence of β_1 and β_2' for $\sigma \ll 1$. Since the first-order Coulomb contribution to the N-electron energy comes from exchange processes between *two* electrons, it must be proportional to $N^2 V_k$, where V_k is the Fourier transform of the Coulomb potential for a characteristic momentum transfer k. In the quantum limit, $k \sim K_F$, so that $N^2 V_k \sim N R_0 r_s^{-1}$: The exchange energy is indeed found to vary as r_s^{-1} [see Eq. (2.7)]. In the Boltzmann limit, $k \sim \lambda_T^{-1}$, so that the exchange energy should be proportional to $k_B T \sigma^3 \rho$, i.e., β_1 should vary as σ^3. The σ dependence of β_2' is not so easy to predict. We will show that $\beta_2' \sim \sigma^{3/2}$. In terms of ρ and r_s, the Coulomb energy $\bar{\varepsilon}_{\text{Coul}}(T)$ eventually reads

$$\bar{\varepsilon}_{\text{Coul}}(T) = R_0(\gamma_1 \rho^2/r_s^3 + \gamma_2 \rho/r_s^{3/2} + \cdots) \tag{2.12}$$

Equation (2.12) is valid for $\rho \ll 1$, whatever r_s is. We can note that, although the Coulomb energy always increases with increasing carrier density, the high-T and $T = 0$ density dependences of $\bar{\varepsilon}_{\text{Coul}}(T)$ are very different.

3. GENERAL FORMALISM

3.1. Thermodynamic Functions

The thermodynamic quantities of a grand canonical ensemble defined by a temperature T and a chemical potential μ are obtained from the grand partition function Ξ

$$\Xi = \operatorname{Tr} e^{-\beta \tilde{H}} \tag{3.1}$$

where $\beta = = 1/k_B T$, $\tilde{H} = \tilde{H}_0 + V$, and $\tilde{H}_0 = H_0 - \mu \hat{N}$, H_0 being the free-particle Hamiltonian, $\hat{N}$ the particle number operator, and V the Coulomb interaction:

$$V = \frac{1}{2} \sum_{q \neq 0} \sum_{p_1, \sigma_1} \sum_{p_2, \sigma_2} V_q C^+_{p_1 + q, \sigma_1} C^+_{p_2, \sigma_2} C_{p_2 + q, \sigma_2} C_{p_1, \sigma_1} \tag{3.2}$$

with $V_q = 4\pi e^2/\varepsilon_0 v q^2$, ε_0 being the static dielectric constant and v the volume of the system.

The thermodynamic potential, average particle number, entropy, and energy are simply related to Ξ by

$$\begin{aligned} \Omega &= -k_B T \ln \Xi, & \bar{N} &= -(\partial \Omega / \partial \mu)_T \\ \bar{S} &= -(\partial \Omega / \partial T)_\mu, & \bar{E} &= \Omega + \mu \bar{N} + T \bar{S} \end{aligned} \tag{3.3}$$

For an N-electron system, the appropriate μ is determined by imposing $\bar{N} = N$.

3.2. V Expansion of the Grand Partition Function

To calculate Ξ, we can think of using the $\tilde{H}$ eigenstates basis.[12] The determination of the $\tilde{H}$ eigenvalues, however, relies on a perturbative expansion for degenerate states, since all the $\tilde{H}_0$ eigenstates but the ground state are degenerate. We can avoid this quite difficult problem by using instead the $\tilde{H}_0$ eigenstates. The V expansion of Ξ then results from the V expansion of $e^{-\beta\tilde{H}}$. It is easily obtained[13] by noting that

$$\frac{d}{d\beta} e^{\beta\tilde{H}_0} e^{-\beta\tilde{H}} = -e^{\beta\tilde{H}_0} V e^{-\beta\tilde{H}} \tag{3.4}$$

so that the $e^{-\beta\tilde{H}}$ expansion comes simply from the iteration of

$$e^{-\beta\tilde{H}} = e^{-\beta\tilde{H}_0} - \int_0^\beta d\beta'\, e^{(-\beta+\beta')\tilde{H}_0} V e^{-\beta'\tilde{H}} \tag{3.5}$$

Let $|l\rangle$ be the eigenstates of H_0 and $\hat{N}$; we set

$$\begin{gathered} H_0 |l\rangle = \varepsilon_l |l\rangle, \qquad \hat{N} |l\rangle = N_l |l\rangle \\ \tilde{\varepsilon}_l = \varepsilon_l - \mu N_l = \sum_{p,\sigma} (\varepsilon_p - \mu)\, n_{p,\sigma}^{(l)} \end{gathered} \tag{3.6}$$

where $\varepsilon_p = \hbar^2 p^2/2m$ and $n_{p,\sigma}^{(l)}$ $(=0$ or $1)$ are the set of filling factors defining $|l\rangle$. Using these $|l\rangle$ states, we find the zeroth- and first-order terms of the grand partition function

$$\Xi_0 = \sum_l \langle l|\, e^{-\beta\tilde{H}_0} \,|l\rangle = \sum_l e^{-\beta\tilde{\varepsilon}_l} \tag{3.7}$$

$$\Xi_1 = \sum_l \langle l| - \int_0^\beta e^{(-\beta+\beta')\tilde{H}_0} V e^{-\beta'\tilde{H}_0} d_{\beta'} \,|l\rangle = -\beta \sum_l V_{ll} e^{-\beta\tilde{\varepsilon}_l} \tag{3.8}$$

In the second-order term given by

$$\Xi_2 = \sum_{l,l'} \langle l| \int_0^\beta d\beta' \int_0^{\beta'} d\beta''\, e^{(-\beta+\beta')\tilde{H}_0} V \,|l'\rangle\langle l'|\, e^{(-\beta'+\beta'')\tilde{H}_0} V e^{-\beta''\tilde{H}_0} \,|l\rangle \tag{3.9}$$

we must differentiate $\tilde{\varepsilon}_l = \tilde{\varepsilon}_{l'}$ and $\tilde{\varepsilon}_l \neq \tilde{\varepsilon}_{l'}$ cases when integrating over β' and β''. It is, however, possible to include these two cases in a compact form:

$$\Xi_2 = -\frac{\beta}{2!} \sum_{l,l'} \left[\frac{V_{ll'} V_{l'l} e^{-\beta\tilde{\varepsilon}_l}}{\tilde{\varepsilon}_l - \tilde{\varepsilon}_{l'}} + (l \leftrightarrow l') \right] \tag{3.10}$$

where $(l \leftrightarrow l')$ stands for the permutation of l and l'. Note that $(\tilde{\varepsilon}_l - \tilde{\varepsilon}_{l'})$ can be replaced by $(\varepsilon_l - \varepsilon_{l'})$, since $\hat{N}$ and V commute. A similar calculation allows us to write the third-order term as

$$\Xi_3 = -\frac{\beta}{3!} \sum_{l,l',l''} \left[\frac{V_{ll'} V_{l'l''} V_{l''l} e^{-\beta \tilde{\varepsilon}_l}}{(\varepsilon_l - \varepsilon_{l'})(\varepsilon_l - \varepsilon_{l''})} + (l \leftrightarrow l' \leftrightarrow l'') \right] \tag{3.11}$$

where $(l \leftrightarrow l' \leftrightarrow l'')$ stands for the five l, l', l'' permutations. [These permutations ensure that the bracket of Eq. (3.11) stays finite when $\varepsilon_{l'}$ or $\varepsilon_{l''}$ goes to ε_l]. Higher-order terms can be calculated along the same lines, although their expressions are somewhat more complicated.

3.3. *V* Expansion of the Thermodynamic Potential

From Eq. (3.3) we can write the Ω expansion as

$$\Omega = -k_B T \ln \Xi_0 - k_B T \ln \left(1 + \sum_{n=1}^{\infty} \frac{\Xi_n}{\Xi_0} \right) = \sum_{n=0}^{\infty} \Omega_n \tag{3.12}$$

(a) Using Eq. (3.7), we find for the zeroth-order term

$$\Omega_0 = -k_B T \ln \Xi_0 = -k_B T \sum_{p,\sigma} \ln[1 + e^{-\beta(\varepsilon_p - \mu)}] \tag{3.13}$$

(b) The first-order term deduced from Eqs. (3.8) is given by

$$\Omega_1 = -k_B T \frac{\Xi_1}{\Xi_0} = -\frac{1}{2} \sum_{p_1 \neq p_2, \sigma_1} V_{p_1 - p_2} f_{p_1} f_{p_2} \tag{3.14}$$

where $f_p = [1 + \exp \beta(\varepsilon_p - \mu)]^{-1}$. This Ω_1 expression is analogous to the usual exchange term of the $T = 0$ energy, the quantum distribution being simply replaced by the Fermi–Dirac finite-T distribution.

(c) The second-order term

$$\Omega_2 = -k_B T \left[\frac{\Xi_2}{\Xi_0} - \frac{1}{2} \left(\frac{\Xi_1}{\Xi_0} \right)^2 \right] = \Omega_{2A} + \Omega_{2D} + \Omega_{2E} \tag{3.15}$$

can be divided into three parts. Since both Ω_1 and Ω_2 have to be proportional to the sample volume v, the $(\Xi_1/\Xi_0)^2$ term of Eq. (3.15), which is proportional to v^2, must be canceled by part of the (Ξ_2/Ξ_0) term. Extracting from Ξ_2 the $l' = l$ term, which reads

$$\Xi_{2A} = \frac{\beta^2}{2} \sum_l e^{-\beta \tilde{\varepsilon}_l} V_{ll}^2 \tag{3.16}$$

we find that $\Omega_{2\mathrm{A}}$ defined as

$$\begin{aligned}\Omega_{2\mathrm{A}} &= -k_{\mathrm{B}}T\left[\frac{\Xi_{2A}}{\Xi_0}-\frac{1}{2}\left(\frac{\Xi_1}{\Xi_0}\right)^2\right]\\ &= -\frac{1}{2k_{\mathrm{B}}T}\sum_{\sigma_1 p_1 \neq (p_2, p_3)} V_{p_1-p_2}V_{p_1-p_3}f_{p_1}(1-f_{p_1})f_{p_2}f_{p_3} \end{aligned}\tag{3.17}$$

is linear in v. The remaining part of Ξ_2, i.e., the sum over the $l' \neq l$ states (which also contains the degenerate states with $\varepsilon_{l'}=\varepsilon_l$), gives rise to a direct term $\Omega_{2\mathrm{D}}$ which reads

$$\Omega_{2\mathrm{D}}=\frac{1}{4}\sum_{q\neq 0} V_q^2 \sum_{p_1\sigma_1 p_2\sigma_2}\left[\frac{f_{p_1}(1-f_{p_1+q})f_{p_2+q}(1-f_{p_2})}{\varepsilon_{p_2+q}+\varepsilon_{p_1}-\varepsilon_{p_2}-\varepsilon_{p_1+q}}+(1\leftrightarrow 2)\right]\tag{3.18}$$

and an exchange term $\Omega_{2\mathrm{E}}$ obtained by replacing *one* factor V_q by $(-V_{p_1-p_2}\delta_{\sigma_1\sigma_2})$. They are both linear in v.

In the following, it will be appropriate to set

$$\varphi_p=f_p(1-f_{p+q}),\qquad \bar{\varphi}_p=f_{p+q}(1-f_p),\qquad \Delta_p=\varepsilon_{p+q}-\varepsilon_p\tag{3.19}$$

This leads to

$$\Omega_{2\mathrm{D}}=\frac{1}{4}\sum_{q\neq 0} V_q^2 I_2(q),\qquad I_2(q)=\sum_{p_1\sigma_1 p_2\sigma_2}\left[\frac{(\varphi_{p_1}+\bar{\varphi}_{p_1})(\varphi_{p_2}-\bar{\varphi}_{p_2})}{2(\Delta_{p_1}-\Delta_{p_2})}+(1\leftrightarrow 2)\right]\tag{3.20}$$

We can easily check that $\Omega_{2\mathrm{A}}$ and $\Omega_{2\mathrm{E}}$ are both finite, while $\Omega_{2\mathrm{D}}$ diverges at low q. This unphysical infinite contribution is compensated by higher-order terms. Indeed, the most diverging nth-order term corresponds to n momentum transfers with the same q. It can be written as

$$\Omega_{n\mathrm{D}}=\frac{1}{2n}\sum_{q\neq 0} V_q^n I_n(q)\tag{3.21}$$

From Eq. (3.11) we find

$$I_3(q)=\frac{1}{2}\sum_{p_1\sigma_1 p_2\sigma_2 p_3\sigma_3}\left[\frac{(\varphi_{p_1}+\bar{\varphi}_{p_1})(\varphi_{p_2}-\bar{\varphi}_{p_2})(\varphi_{p_3}-\bar{\varphi}_{p_3})}{(\Delta_{p_1}-\Delta_{p_2})(\Delta_{p_1}-\Delta_{p_3})}+(1,2,3)\right]\tag{3.22}$$

where (1, 2, 3) stands for the two other *circular* permutations of 1, 2, and 3. Figure 2 shows the Feynman diagrams representing $\Omega_{2\mathrm{A}}$, $\Omega_{2\mathrm{E}}$, $\Omega_{n\mathrm{D}}$ as well as other terms of the thermodynamic potential expansion. The $\Omega_{n\mathrm{D}}$ (Fig. 2d) correspond to the random phase approximation (RPA). Using

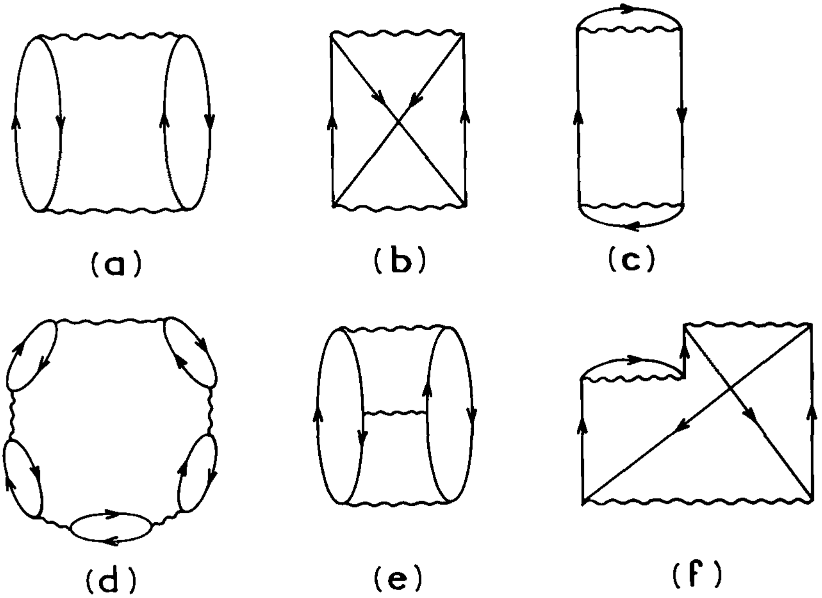

Fig. 2. Feynman diagrams contributing to the correlation thermodynamic potential. (a) The second-order direct term (Ω_{2D}); (b) the second-order exchange term (Ω_{2E}); (c) the Ω_{2A} contribution; (d) the RPA nth-order term (Ω_{nD}); (e, f) other third-order terms. Solid lines represent electron propagators, while wavy lines represent Coulomb interaction.

the finite-T Green's function formalism, we can recover(3,8) the above expressions of Ω_{2A}, Ω_{2E}, Ω_{2D}, and Ω_{3D}. For Ω_{nD}, we get

$$I_n(q) = \frac{1}{2} \sum_{p_1\sigma_1 \cdots p_n\sigma_n} \left[\frac{(\varphi_{p_1} + \bar{\varphi}_{p_1})(\varphi_{p_2} - \bar{\varphi}_{p_2}) \cdots (\varphi_{p_n} - \bar{\varphi}_{p_n})}{(\Delta_{p_1} - \Delta_{p_2}) \cdots (\Delta_{p_1} - \Delta_{p_n})} + (1, 2, 3, \dots, n) \right] \tag{3.23}$$

The Ω_{nD} summation produces a finite contribution to Ω, as physically expected, since it generates a low-q cutoff, equivalent to a Coulomb interaction screening. However, as the low-q behavior of $I_n(q)$ is different in the high-T limit and in the $T = 0$ limit, we must consider these two cases separately.

4. HIGH-TEMPERATURE LIMIT

For high-T, the Fermi distribution reduces to the Boltzmann distribution, $f_p \approx \exp[-\beta(\varepsilon_p - \mu)]$, μ and T being such that $\gamma = e^{\beta\mu} \ll 1$. In this high-$T$ limit, a V expansion has no meaning unless the characteristic

Coulomb energy R_0 is much smaller[3] than the mean kinetic energy $k_B T$; this implies $\rho = \lambda_T / a_0 \ll 1$. In this small-$\rho$ limit, the chemical potential μ is very close to the noninteracting gas chemical potential μ_T, Eq. (2.10), so that the condition $\gamma \ll 1$ is equivalent to the usual condition of the Boltzmann limit $\sigma = \lambda_T / d \ll 1$. The domain of validity of the results of this paragraph thus corresponds to the domain II of the (ρ, r_s) plane (see Fig. 1). Note that the above conditions do not imply $r_s = d/a_0$ smaller than 1.

4.1. Thermodynamic Potential

For $\gamma \ll 1$, the zeroth-order potential, Eq. (3.13), reads

$$\Omega_0 = -k_B T \bar{N}_0, \qquad \bar{N}_0 = -\left(\frac{\partial \Omega_0}{\partial \mu}\right)_T = \sum_{p\sigma} f_p \approx \frac{2\gamma v}{\lambda_T^3} \tag{4.1}$$

where $\bar{N}_0$ is the zeroth-order mean particle number. The first-order term, Eq. (3.14), can be written as

$$\Omega_1 = (1/4\pi)\, \rho\gamma\Omega_0 \tag{4.2}$$

Turning to second-order terms, we find from dimensional arguments that

$$\Omega_{2A} \sim \frac{1}{k_B T}\left(\frac{e^2}{\varepsilon_0 v K_T^2}\right)^2 \bar{N}_0^3 \sim \rho^2 \gamma^2 \Omega_0 \tag{4.3}$$

as the characteristic momentum scale in this limit is $K_T = \lambda_T^{-1}$. Since $f_p \ll 1$, we can replace φ_p by f_p and $\bar{\varphi}_p$ by f_{p+q} in Ω_{2D} and Ω_{2E}. It is easy to check that Ω_{2E} stays finite in the $q = 0$ limit, so that, from dimensional arguments, we get

$$\Omega_{2E} \sim v K_T^3 \left(\frac{e^2}{\varepsilon_0 v K_T^2}\right)^2 \frac{\bar{N}_0^2}{\hbar^2 K_T^2/m} \sim \rho^2 \gamma \Omega_0 \tag{4.4}$$

(the vK_T^3 factor comes from the sum over q). On the contrary, Ω_{2D} diverges for $q \to 0$. More precisely, in the low-q limit, $\varphi_p \sim \bar{\varphi}_p \sim f_p(1 - f_p) = kT\, \partial f_p / \partial \mu$ while $\varphi_p - \bar{\varphi}_p \sim \Delta_p\, \partial f_p / \partial \mu$, so that we get from Eq. (3.23)

$$\lim_{q \to 0} I_n(q) = -kT \left(\frac{\partial \bar{N}_0}{\partial \mu}\right)^n \qquad \text{for} \quad n \geqslant 2 \tag{4.5}$$

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[3] Let us stress that the high-T limit considered here is not the usual "classical" limit in which $\hbar \to 0$, so that μ_F and $\sigma \to 0$ while $R_0, \rho, r_s \to \infty$. In this classical limit, the first term of Eq. (2.12) vanishes. The second term of Eq. (2.12) is nothing but the Debye–Hückel result, valid in the weak-coupling limit, i.e., when $e^2/dk_B T \sim \rho\sigma \ll 1$.

We conclude that, for $T \neq 0$, $\Omega_{n\mathrm{D}}$ diverges as q^{-2n+2}. More precisely, we find

$$\Omega_{n\mathrm{D}} \sim -\frac{v k_{\mathrm{B}} T}{4\pi^2} \int q^2\, dq\, \frac{1}{n} \left(-\frac{q_s^2}{q^2} \right)^n \tag{4.6}$$

where q_s is given by[4]

$$q_s = \left[\frac{4\pi e^2}{\varepsilon_0} \, \frac{\partial}{\partial \mu} \left(\frac{\bar{N}_0}{v} \right) \right]^{1/2} = 2\rho^{1/2}\gamma^{1/2} K_T \ll K_T \tag{4.7}$$

The sum of all $\Omega_{n\mathrm{D}}$ terms thus reduces to a convergent integral[5]

$$\begin{aligned} \Omega_{\mathrm{D}} &= \sum_{n=2}^{\infty} \Omega_{n\mathrm{D}} \\ &\sim \frac{v k_{\mathrm{B}} T}{4\pi^2} \int_0^1 \frac{d\lambda}{\lambda} \int_0^\infty q^2\, dq\, \frac{\lambda^2 (q_s^2/q^2)^2}{1 + \lambda q_s^2/q^2} \\ &= -\frac{v k_{\mathrm{B}} T}{12\pi} q_s^3 \\ &= \Omega_0 \left[\left(\frac{1}{3\pi} \right) \rho^{3/2} \gamma^{1/2} + O(\rho^2 \gamma) \right] \end{aligned} \tag{4.8}$$

Ω_{D} is proportional to $\rho^{3/2}$, i.e., to e^3, and not to e^4 like the two second-order (finite) terms $\Omega_{2\mathrm{A}}$ and $\Omega_{2\mathrm{E}}$. Other diverging contributions also appear in the higher-order terms. We can show that the larger ones give a contribution of the order of $\rho\gamma\Omega_{\mathrm{D}}$.

Adding the three first leading contributions to the thermodynamic potential, Eqs. (4.1), (4.2), and (4.8), we get

$$\Omega = -k_{\mathrm{B}} T \bar{N}_0 [1 + (1/4\pi)\, \rho\gamma + (1/3\pi)\, \rho^{3/2}\gamma^{1/2} + O(\rho^2\gamma)] \tag{4.9}$$

4.2. Average Energy

From Ω, we obtain the average energy, using Eq. (3.3). We get

$$\bar{E}(T, \mu) = k_{\mathrm{B}} T \bar{N}_0 [3/2 + (1/4\pi)\, \rho\gamma + (1/4\pi)\, \rho^{3/2}\gamma^{1/2} + O(\rho^2\gamma)] \tag{4.10}$$

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[4] To lowest order in ρ, Eq. (4.7) is identical to Eq. (2.6) and the q_s cutoff reduces to the Debye–Hückel screening wavevector, since in this limit $\bar{N}_0 = N$ and $\mu = \mu_T$, as shown later.

[5] From Eq. (4.8) we can check that the dominant contribution to Ω_{D} comes from $q \sim q_s \ll K_T$, so that we may use the low-q limiting values of $I_n(q)$ in the whole range of integration.

In order to get $\bar{E}(T, N)$, we must calculate $\mu(T, N)$ by setting $\bar{N}(\mu) = N$. From Eq. (4.9) we find

$$N = -(\partial\Omega/\partial\mu)_T = \bar{N}_0[1 + (1/2\pi)\,\rho\gamma + (1/2\pi)\,\rho^{3/2}\gamma^{1/2} + O(\rho^2\gamma)] \qquad (4.11)$$

To zeroth order in ρ, $N = \bar{N}_0$ and $\gamma = \gamma_0 = e^{\beta\mu_T} = (3\sigma^3/8\pi)$. To second order in ρ, Eq. (4.11) thus gives

$$\bar{N}_0 = N[1 - (1/2\pi)\,\rho\gamma_0 - (1/2\pi)\,\rho^{3/2}\gamma_0^{1/2} + O(\rho^2\gamma_0)]$$

This transforms Eq. (4.10) into

$$\bar{\varepsilon}(T) = \frac{\bar{E}}{N} R_0 \left[\frac{6\pi}{\rho^2} - \frac{3}{4\pi}\frac{\sigma^3}{\rho} - \left(\frac{3}{2\pi}\right)^{1/2}\frac{\sigma^{3/2}}{\rho^{1/2}} + O(\rho^0\sigma^3)\right] \qquad (4.12)$$

Note that the correlation terms is exactly equal to the Debye–Hückel result of the classical limit$^{(3,6,7),6}$: Indeed in this $\hbar \approx 0$ limit, Eq. (4.12) reduces to its first and third terms.

Since $\sigma = \rho/r_s$ depends on both density and temperature, it can be interesting to reexpress the average Couolomb energy as

$$\bar{\varepsilon}_{\text{Coul}}(T) = R_0\left[-\frac{3}{4\pi}\frac{\rho^2}{r_s^3} - \left(\frac{3}{2\pi}\right)^{1/2}\frac{\rho}{r_s^{3/2}} + O\left(\frac{\rho^3}{r_s^3}\right) + \cdots\right] \qquad (4.13)$$

Here, the density appears in r_s only, while the temperature appears in ρ only. Let us stress that the above equations does not result from a small-r_s expansion, but from a *small-ρ expansion*, so that it can be valid for $r_s > 1$: the two conditions $\rho \ll 1$ and $\sigma \ll 1$ correspond to

$$\rho = \lambda_T/a_0 \ll \min(1, r_s) \Leftrightarrow k_B T \gg \max(R_0, \mu_F \sim R_0/r_s^2) \qquad (4.14)$$

whatever r_s is; so that the range of temperature for Eq. (4.13) to be valid is larger for $r_s > 1$ than for $r_s < 1$ (see Fig. 1).

We see that the Coulomb energy vanishes for hot dilute carriers. This effect is, however, stronger on the exchange term than on the correlation term: The correlation energy is the largest at very high T, i.e., for $\rho < r_s^{3/2}$ (region II_b of Fig. 1). If $r_s > 1$, this condition is *always* fulfilled in the range of validity of the Boltzmann limit result. If $r_s < 1$, the correlation energy dominates the exchange energy at very high T only $[k_B T > \mu_F(\mu_F/R_0)^{1/2}]$. At smaller temperature $[\mu_F < k_B T < \mu_F(\mu_F/R_0)^{1/2}]$ (region II_a of Fig. 1), the exchange energy is the largest. This result has to be contrasted with the $T = 0$ situation in which the exchange energy is the dominant term of the Coulomb contributions.

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[6] See footnote 3.

5. $T=0$ LIMIT

The $T=0$ limit of the energy expansion can of course be deduced$^{(3)}$ from the finite-T approach given in Section 3. This derivation is instructive, as it allows one to grasp the differences between the low-T and high-T behaviors.

5.1. Thermodynamic Potential

The zeroth-order term is obtained from the $T=0$ limit of Eq. (3.13):

$$\begin{aligned} \Omega_0 &= \sum_{p,\sigma} (\varepsilon_p - \mu)\, \Theta(\mu - \varepsilon_p) = -(2/5)\, \mu \bar{N}_{00} \\ \bar{N}_{00} &= -(\partial \Omega_0 / \partial \mu)_T = (v/3\pi^2)(2m\mu/\hbar^2)^{3/2} \end{aligned} \tag{5.1}$$

Since $f_p = \Theta(\mu - \varepsilon_p)$, the first-order potential, Eq. (3.14), reads

$$\Omega_1 = (15/4\pi)\, r \Omega_0, \qquad r = (R_0/\mu)^{1/2} \tag{5.2}$$

Note that, as we are working with μ instead of N, the parameter which appears in the V expansion is r instead of r_s. Turning to the higher-order contributions, we see that $\Omega_{n\mathrm{D}}$, Eq. (3.21), also diverges when $T=0$. However, it is less divergent at $T=0$ than at high T, since $I_n(q)$, Eq. (3.23), is now of the order of q instead of $(q)^0$: As $f_p(1-f_p) \equiv 0$ for a step function, φ_p and $\bar{\varphi}_p$ both vanish in the $q=0$ limit. The n factors of the numerator of $I_n(q)$ restrict each p integration to momenta within q from the Fermi surface, so that

$$\lim_{q \to 0} I_n(q) \propto (v K_0^3)^n \frac{(q/K_0)^n}{(\hbar^2 q K_0/m)^{n-1}} \propto q \tag{5.3}$$

where $K_0 = (2m\mu/\hbar^2)^{1/2}$ is the $T=0$ characteristic momentum. This leads to[7]

$$\Omega_{n\mathrm{D}} \sim C_n \Omega_0 \int \frac{q^3\, dq}{K_0^4} \left(-\frac{q_{s0}^2}{q^2} \right)^n \tag{5.4}$$

$$q_{s0} = \left[\frac{4\pi e^2}{\varepsilon_0} \frac{\partial}{\partial \mu} \left(\frac{\bar{N}_{00}}{v} \right) \right]^{1/2} = \left(\frac{4r}{\pi} \right)^{1/2} K_0 \ll K_0 \tag{5.5}$$

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[7] To lowest order in r_s, Eq. (5.5) is identical to Eq. (2.6) and the q_{s0} cutoff reduces to the Thomas–Fermi screening wavevector, since in this limit $\bar{N}_{00} = N$ and $\mu = \mu_{\mathrm{F}}$, as shown later.

The C_n are numerical prefactors. The sum of these $\Omega_{n\mathrm{D}}$ reads

$$\Omega_D \sim \frac{16}{\pi^2} C_2 r^2 \Omega_0 \int \frac{dq}{q}\left[1 - \frac{C_3}{C_2}\left(\frac{q_{s0}}{q}\right)^2 + \frac{C_4}{C_2}\left(\frac{q_{s0}}{q}\right)^4 + \cdots\right] \tag{5.6}$$

The precise summation of these RPA terms can be obtained following Gell-Mann and Brueckner.(1) We note, however, that the Ω_D leading term can be obtained without calculating the C_n for $n > 2$: If Ω_D is finite as expected for physical reasons, the bracket in Eq. (5.6) has to go to zero in the $q = 0$ limit. It thus produces an effective cutoff to the logarithmic singularity of the order of q_{s0}. Consequently, the Ω_D leaning term must be

$$\Omega_\mathrm{D} \sim -(16/\pi^2)\, C^2 r^2 \Omega_0 \ln(q_{s0}/K_0) \tag{5.7}$$

A straightforward calculation of $I_2(q)$, Eq. (3.20), gives $C_2 = 5(1 - \ln 2)/8$.

As in the high-T limit, the two other second-order terms $\Omega_{2\mathrm{A}}$ and $\Omega_{2\mathrm{E}}$ (both of the order of r^2), as well as all the other divergent terms appearing in Ω_n for $n \geqslant 3$ (of the order of $r^3 \ln r$), are smaller than Ω_D for $r \ll 1$. Consequently, the three first terms of the Ω expansion read

$$\Omega = \bar{N}_{00}\mu\left[-\frac{2}{5} - \frac{3}{2\pi} r + \frac{2}{\pi^2}(1 - \ln 2) r^2 \ln r + O(r^2)\right] \tag{5.8}$$

5.2. Average Energy

By imposing $\bar{N}(\mu) = -\partial\Omega/\partial\mu = N$, we can write μ as

$$\mu = \mu_\mathrm{F}[1 + a_1 r_0 + a_2 r_0^2 \ln r_0 + O(r_0^2)] \tag{5.9}$$

where $r_0 = (R_0/\mu_\mathrm{F})^{1/2} = (4/9\pi)^{1/3} r_s$. Actually, we do not need to claculate a_1 and a_2, as long as we are interested in the correlation energy leading term, since we have

$$\begin{aligned}\bar{E}(T=0) &= \Omega + \mu N \\ &= \Omega_0(\mu_\mathrm{F}) + (\mu - \mu_\mathrm{F})(\partial\Omega_0/\partial\mu)_{\mu_\mathrm{F}} + \Omega_1(\mu_\mathrm{F}) + \Omega_\mathrm{D}(\mu_\mathrm{F}) + \mu N + O(r_0^2) \\ &= E_0 + \Omega_1(\mu_\mathrm{F}) + \Omega_\mathrm{D}(\mu_\mathrm{F}) + O(r_0^2)\end{aligned} \tag{5.10}$$

E_0 is just the ground-state energy of N free electrons: $E_0 = \Omega_0(\mu_\mathrm{F}) + N\mu_\mathrm{F} = (3/5)\, N\mu_\mathrm{F}$. Equation (5.10) shows that in the $T = 0$ limit, the exchange and correlation *leading term* of the energy are equal to the exchange and correlation terms of the thermodynamic potential calculated with the *unperturbed* chemical potential μ_F, i.e., with $r=r_0$. We thus recover the well-known result

$$\bar{\varepsilon}_{\text{Coul}}(T=0)=R_0\left[-\frac{3}{2\pi}\left(\frac{9\pi}{4}\right)^{1/3}\frac{1}{r_s}+\frac{2}{\pi^2}(1-\ln 2)\ln r_s+O(r_s^0)\right] \qquad (5.11)$$

For completeness we wish to stress that if we want to go beyond the ($\ln r_s$) term of Eq. (5.11), it is much simpler to calculate the ground-state energy directly than to derive it form the thermodynamic potential. Within this direct approach, the r_s^2 term of the ground-state energy [which corresponds to the r_s^0 term in Eq. (5.11)] simply originates from the exchange second-order term and from the r_s^2 part of the RPA summation. Within the Ω approach, in addition, we must take into account the Ω_{2A} term (which has no equivalent in the ground-state energy); we also need to calculate μ up to the order of r_s^2, to insert this result into the different $\Omega_0(\mu)$, $\Omega_1(\mu)$,... constributions, and to collect all the r_s^2 terms. Although the finite-T approach is clearly not the simplest way to get the $T=0$ energy, the derivation of the $T=0$ and high-T results using the same formalism allows us to see clearly the origin of the change from the $e^4 \ln\ e^2$ to e^3 dependence of the correlation energy leading term.

We can end this part by considering the correlation energy in the *small-T* limit. The e dependence of its leading term is directly related to the small-q dependence of $I_2(q)$. We have shown that $I_2(q)$ behaves as $(q)^1$ for $T=0$ and as $(q)^0$ at high T. In fact, a $(q)^0$ term does exist in $I_n(q)$ once T is not strictly zero [see Eqs. (4.5)], the prefactor of this $(q)^0$ term canceling with T in the small-T limit. The summation of these $(q)^0$ terms can be performed as for high T: Eqs. (4.5)–(4.8) are still valid provided that $\bar{N}_0$ and q_s are replaced by their small-T limits $\bar{N}_{00}$ and q_{s0}. The resulting e^3 term of Ω_D is

$$\Omega_D=-Nk_BT\frac{2}{\sqrt{\pi}}\left(\frac{R_0}{\mu_F}\right)^{3/4}=-NR_0\left(\frac{16}{3}\frac{1}{\sigma^2\sqrt{r_s}}\right) \qquad (5.12)$$

It cancels with T as expected and leads to a correlation energy term which reads

$$\Delta\bar{\varepsilon}_{\text{Coul}}=R_0\left[\frac{1}{\pi}\left(\frac{9\pi}{4}\right)^{2/3}\frac{1}{\sqrt{r_s}}\left(\frac{k_BT}{\mu_F}\right)\right] \qquad (5.13)$$

At small T, the correlation energy dominant terms are thus composed of the $e^4 \ln e^2$ term of the $T=0$ limit (with a T-dependent prefactor) plus this Te^3 term. We see that this new term starts to play a role for $k_BT/\mu_F \geqslant \sqrt{r_s}\ln r_s$.

6. CONCLUSION

We have rederived the Coulomb energy expansion at finite temperature starting from scratch, i.e., using only statistical physics first principles. In both the high-T and the $T=0$ limits, we recover the first two leading terms of this energy in a simple way. At high T we find that for $\rho \ll \min(1, r_s) \Leftrightarrow k_B T \gg \max(R_0, \mu_F \sim R_0/r_s^2)$ the average Coulomb energy reads

$$\bar{\varepsilon}_{\text{Coul}}(T) = R_0 \left[-0.239 \frac{\rho^2}{r_s^3} - 0.691 \frac{\rho}{r_s^{3/2}} + O\left(\frac{\rho^3}{r_s^3}\right) \right] \tag{6.1}$$

r_s and ρ being the interparticle distance and thermal length in Bohr radius units. At $T=0$, the Coulomb energy reads, for $r_s \ll 1$,

$$\bar{\varepsilon}_{\text{Coul}}(T=0) = R_0 \left[-\frac{0.916}{r_s} + 0.0622 \ln r_s + O(r_s^0) \right] \tag{6.2}$$

The first term of $\bar{\varepsilon}_{\text{Coul}}(T)$, always proportional to e^2, is the exchange energy. The second term, which is the leading contribution to the correlation energy, is proportional to e^3 for high T and to $e^4 \ln e^2$ for $T=0$. It comes from a second-order divergent term screened by other higher-order divergent terms. The screening generated by this summation is nothing but the usual Thomas–Fermi (resp. Debye–Hückel) screening for degenerate (resp. nondegenerate) electrons. The different e^2 behaviors at low T and high T originate from the fact that the second-order Coulomb processes are more divergent for high T than for $T=0$. We have also shown that an e^3 term in the correlation energy does appear once T is not strictly zero, the prefactor of this term canceling as T in the small-T limit.

We note that the correlation term can be larger than the exchange term at very high temperature (while it is always smaller at $T=0$). This may appear surprising since correlation processes are of higher order in the Coulomb interaction. The importance of these correlation processes at high T comes from the fact that in this limit all electrons participate in small momentum excitations, while only electrons close to the Fermi surface are involved at $T=0$.

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