

Specific Heat of a Degenerate Electron Gas at High Density

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The methods of the preceding paper of Gell-Mann and Brueckner are generalized so that not only the ground state but also the low excited states of an electron gas can be discussed. The energy levels relative to the ground state are the same as those of a gas of independent particles where the energy of each particle (in rydbergs) is a certain function $W(p)$ of its momentum (expressed in units of the Fermi momentum). The specific heat of the gas at low temperature is proportional to the density of single particle levels at the surface of the Fermi sea, or inversely proportional to $(dW/dp)_{p=1}$. This last quantity is calculated for high density (small r_s , where density is proportional to r_s^{-3}) and compared to the corresponding quantity for a free electron gas. The ratio is found to be $1+0.083r_s[-\ln r_s-0.203]$ +higher terms in r_s . The expansion is exact and may be compared with the approximate result of Pines, who finds $1+0.083r_s[-\ln r_s+1.47]+\dots$.

IN the preceding paper,¹ to be referred to as I, the energy of the ground state of an electron gas is computed at high density. Here we shall treat the energies of low excited states by the same method and thus calculate the low-temperature specific heat at high density.

We may label the states by referring them to corresponding states of a free-electron gas. The familiar methods of perturbation theory (suitably modified to fit the problem) will convert a given energy eigenstate Φ_n of the system of free electrons into an energy eigenstate Ψ_n of the system with Coulomb interactions among the electrons. We shall be concerned, of course, with the perturbed energy E_n associated with Ψ_n , and not with the unperturbed (purely kinetic) energy associated with Φ_n . Nevertheless, we shall refer to the n th state by describing the *unperturbed* state Φ_n .

Thus we shall speak of the ground state as that in which all one-particle momentum states inside the Fermi sphere are occupied and all those outside are unoccupied. This is, of course, a description of the unperturbed ground state Φ_0 . But when we speak of the energy E_0 of the ground state, we shall mean the perturbed energy associated with the exact eigenstate Ψ_0 of the interacting system.

Similarly, we shall specify an excited state by listing the momenta and spins $\{\mathbf{p}_j, s_j\}$ (with $j=1, \dots, \nu$) of the vacated one-particle states inside the Fermi sphere and the momenta $\{\mathbf{k}_j\}$ of the occupied one-particle states outside the sphere. (The momenta are expressed in units of the Fermi momentum P .) Again we are describing an unperturbed state; and again, in speaking of the energy, we shall mean the energy E of the perturbed state.

As in I, we consider a macroscopic sample of gas; the number N of electrons is very large, say $\sim 10^{23}$. We now restrict ourselves to treating those states of the gas in which the number ν of excited particles is small

compared to N . At low temperatures, only such states will be important. For these states of the electron gas, the energy E (in units of the rydberg) may be written in the form

$$E = E_0 + \sum_{j=1}^{\nu} \{W(k_j) - W(p_j)\} + O(\nu/N). \quad (1)$$

This can be done because the interaction energy of the excited particles among themselves is of order ν/N compared to their interaction energy with the rest of the gas. Under our assumptions the term of order ν/N can be neglected, and the specific heat at low temperature depends only on the form of the function $W(p)$.

Thus, for the computation of the specific heat at low temperatures, we are justified in treating the interacting electron gas as a system of independent particles obeying Fermi-Dirac statistics and with the energy (in rydbergs) of each given as a function of momentum (in units of P) by $W(p)$. It is well known² that under these conditions the specific heat C per electron at constant volume is proportional to the density of "one-particle energy levels" at the surface of the Fermi sphere, that is, proportional to $[(dW/dp)_{p=1}]^{-1}$.

For a free-electron gas, we have]

$$W_F(p) = \frac{p^2 P^2 \left[\frac{e^4 m}{2m} \right]^{-1}}{2m \left[2\hbar^2 \right]} = p^2 / \alpha^2 r_s^2, \quad (2)$$

and

$$[(dW_F/dp)_{p=1}]^{-1} = \alpha^2 r_s^2 / 2, \quad (3)$$

where, as in I, $(4/3)\pi r_s^3$ is the volume per electron (in units of the Bohr radius cubed) and α is $(4/9\pi)^{1/2}$. The specific heat of a free-electron gas at low temperature is given by a familiar formula,³ which we write as follows:

$$C_F(T, r_s) = m^{-1} \hbar^2 e^{-4} K^2 T \cdot \alpha^2 r_s^2, \quad (4)$$

where T is temperature and K is Boltzmann's constant.

Evidently the formula for the low-temperature spe-

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¹ M. Gell-Mann and K. A. Brueckner, Phys. Rev. **106**, 364 (1957), preceding paper.

² D. Pines, in *Solid State Physics* (Academic Press, Inc., New York, 1955), Vol. 1, p. 367.

³ F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York 1940), p. 150.

cific heat of an electron gas with interactions is

$$C(T, r_s) = m^{-1} \hbar^2 e^{-4K^2 T} \cdot 2 \left[(dW/dp)_{p=1} \right]^{-1}. \quad (5)$$

and in (4) we have the special case of free electrons, for which $W = W_F$. Our remaining task is to calculate $W(p)$ (or at least dW/dp at $p=1$) at high density for an electron gas with Coulomb interactions.

We may think of $W(p)$ in the following way: We consider the ground state of the gas, in which the filled one-particle states are those inside the Fermi sphere. We now examine the change in the energy (exact or perturbed energy) of the system when one electron, with momentum \mathbf{p} , is annihilated. (Clearly $p \leq 1$ here.) Then $W(p)$ is the energy lost in the annihilation, to within any additive constant. Similarly, if we start with the gas in its ground state and create an electron of momentum \mathbf{k} ($k \geq 1$), then $W(k)$ is the energy gained in the creation. This interpretation of the quantity W is evidently consistent with Eq. (1).

Now in I we have treated the perturbation series for the ground state energy per particle, ϵ (in rydbergs). The fact that the terms of the series diverge is of no importance, since we have shown how to cure the divergence. In each term of the series for the ground state energy, there are sums over occupied one-particle states with momenta \mathbf{p}_i such that $p_i \leq 1$ and over unoccupied states with momenta \mathbf{k}_i (equal, say, to $\mathbf{p}_i + \mathbf{q}$) such that $k_i > 1$. For example, see Eqs. (9), (10), and (11) of reference 1. (We shall refer to these as I-9, I-10, etc.)

If a particle with momentum \mathbf{p} and spin s is annihilated, the only change in the perturbation series for the ground state energy consists in amending the condition " $p_i \leq 1$ " for an occupied state by inserting the exception " $\mathbf{p}_i \neq \mathbf{p}$ if $s_i = s$ " and amending the condition " $k_i > 1$ " for an occupied state by allowing \mathbf{k}_i to equal \mathbf{p} if $s_i = s$. The number of occupied states is decreased by one and that of unoccupied ones correspondingly increased. The resulting energy change can best be discussed by means of an example.

One term in the series for the ground state energy per particle is given in Eq. (I-8):

$$\epsilon_a^{(2)} = -\frac{3}{8\pi^5} \int \frac{d^3q}{q^4} \int_{\substack{p_1 < 1 \\ |\mathbf{p}_1 + \mathbf{q}| > 1}} d^3p_1 \int_{\substack{p_2 < 1 \\ |\mathbf{p}_2 + \mathbf{q}| > 1}} d^3p_2 \times \frac{1}{q^2 + \mathbf{q} \cdot (\mathbf{p}_1 + \mathbf{p}_2)}. \quad (\text{I-8})$$

If we multiply $\epsilon_a^{(2)}$ by N , the number of electrons, we obtain the corresponding term in the total energy of the ground state, at least to order N . We may write N as $2\Omega(2\pi)^{-3}4/3\pi$, where Ω is the volume of the gas in units of $\hbar^3 P^{-3}$ and the factor of 2 comes from the two spin states. Furthermore, we may replace the integral over \mathbf{p}_1 , say, by $\Omega^{-1}(2\pi)^3$ times a sum over \mathbf{p}_1 . We have, then, for the part of the total ground state energy

corresponding to $\epsilon_a^{(2)}$:

$$E_a^{(2)} = -2 \cdot \frac{4}{3} \pi \left(\frac{3}{8\pi^5} \right) \int \frac{d^3q}{q^4} \sum_{\substack{p_1 < 1 \\ |\mathbf{p}_1 + \mathbf{q}| > 1}} \int_{\substack{p_2 < 1 \\ |\mathbf{p}_2 + \mathbf{q}| > 1}} d^3p_2 \times \frac{1}{q^2 + \mathbf{q} \cdot (\mathbf{p}_1 + \mathbf{p}_2)}. \quad (6)$$

Now let us remove from the gas a particle with spin up and momentum \mathbf{p} . There are four contributions to the loss of energy:

(a) For *one* of the spin states, the term $\mathbf{p}_1 = \mathbf{p}$ is dropped from the sum. (The one-particle state with momentum \mathbf{p} and spin up is no longer occupied.)

(b) For *one* of the spin states, a term $\mathbf{p}_1 + \mathbf{q} = \mathbf{p}$ is added to the sum. (The one-particle state with momentum \mathbf{p} and spin up is now among the unoccupied ones.)

(c) and (d) Corresponding contributions from the sum or integral over \mathbf{p}_2 rather than \mathbf{p}_1 . These are evidently equal to (a) and (b).

We have, then, for the contribution $W_a^{(2)}$ of this process to the total energy removed, the expression

$$W_a^{(2)} = -2 \cdot \frac{4}{3} \pi \frac{3}{8\pi^5} \left\{ \int_{|\mathbf{p} + \mathbf{q}| > 1} \frac{d^3q}{q^4} \int_{\substack{p_2 < 1 \\ |\mathbf{p}_2 + \mathbf{q}| > 1}} d^3p_2 \times \frac{1}{q^2 + \mathbf{q} \cdot (\mathbf{p} + \mathbf{p}_2)} - \int_{|\mathbf{p} - \mathbf{q}| < 1} \frac{d^3q}{q^4} \int_{\substack{p_2 < 1 \\ |\mathbf{p}_2 + \mathbf{q}| > 1}} d^3p_2 \times \frac{1}{\mathbf{q} \cdot (\mathbf{p} + \mathbf{p}_2)} \right\}, \quad (7)$$

where the factor 2 in front is really the product of three factors: 2 from the two spin states as in (6); $\frac{1}{2}$ from the selection of spin up only; and 2 from the existence of (c) and (d) in addition to (a) and (b).

By an obvious generalization of this method, we can compute the contribution to $W(p)$ corresponding to each term in ϵ that we investigated in I. The contribution $W_F(p)$ corresponding to the Fermi energy ϵ_F is already given by (2). We must take up next the term $W_x(p)$ corresponding to ϵ_x , the exchange energy. The expression (I-2) for ϵ_x comes from the more explicit formula

$$\epsilon_x = -\frac{3}{8\pi^3} \frac{1}{\alpha r_s} \int_{p_1 < 1} d^3p_1 \int_{p_2 < 1} d^3p_2 \frac{1}{(\mathbf{p}_1 + \mathbf{p}_2)^2}. \quad (8)$$

The method outlined above then gives at once

$$W_x(p) = -2 \cdot \frac{4}{3} \pi \cdot \frac{3}{8\pi^3} \frac{1}{\alpha r_s} \int_{p_2 < 1} d^3p_2 \frac{1}{(\mathbf{p} + \mathbf{p}_2)^2}. \quad (9)$$

Now let us attempt to compute $(dW/dp)_{p=1}$ as a series of ascending powers of r_s . The leading term is of course $(dW_F/dp)_{p=1} = 2/(\alpha^2 r_s^2)$ and the next one should be $(dW_x/dp)_{p=1}$, presumably of order $1/r_s$. However, this comes out logarithmically divergent.⁴ In fact, the situation encountered in I is repeated here, a series of increasing divergences but each occurring one order earlier than in I. Corresponding to Eq. (I-7), we have

$$\left(\frac{dW}{dp}\right)_{p=1} = \frac{2}{\alpha^2 r_s^2} + \frac{1}{r_s} (\log \text{divergence}) + \frac{1}{r_s^2} (\text{quadratic div}) + \dots \quad (10)$$

Again, as in I, we expect that the divergent integrals, when summed, will cut themselves off at $q_{\min} \sim r_s^{1/2}$, so that in place of (10) we shall find

$$\left(\frac{dW}{dp}\right)_{p=1} = \frac{2}{\alpha^2 r_s^2} + \frac{1}{r_s} (B \ln r_s + D) + \text{higher terms in } r_s. \quad (11)$$

In order to obtain this form, we must, as in I, sum the leading divergence in each order. Moreover, the leading divergence in each order beyond the first is supplied by precisely the same process as in I, since the cause of divergence is still the piling-up of factors $1/q^2$ coming from successive Coulomb interactions with the same momentum transfer. So from just the processes considered in I, we can obtain *exact* values of B and D . Moreover, in all orders beyond the first, we may employ the crudest approximation that preserves the leading divergence. In particular, in second order, we may ignore $W_b^{(2)}$ compared to $W_a^{(2)}$, which alone has a quadratic divergence in $(dW/dp)_{p=1}$.

The series that we must examine, then, is $W_x + W_a^{(2)} + W^{(3)} + W^{(4)} + \dots$, where these terms correspond precisely to $\epsilon_x, \epsilon_a^{(2)}, \epsilon^{(3)}, \epsilon^{(4)}$, etc., of I. We have already calculated W_x and $W_a^{(2)}$, and we may now study the derivatives of these terms at $p=1$. For the first-order term W_x we have, from (9),

$$W_x = -\frac{1}{\pi^2 \alpha r_s} \int \frac{d^3 q}{q^2} \eta(1 - |\mathbf{p} + \mathbf{q}|), \quad (12)$$

where $\eta(x)$ is unity for positive x and zero for negative x . The derivative is then

$$\left(\frac{dW_x}{dp}\right)_{p=1} = \frac{1}{\pi^2 \alpha r_s} \int \frac{d^3 q}{q^2} \delta(1 - |\mathbf{n} + \mathbf{q}|) \mathbf{n} \cdot (\mathbf{n} + \mathbf{q}), \quad (13)$$

where \mathbf{n} is a unit vector in the direction of \mathbf{p} . We may put $\mathbf{n} + \mathbf{q}$ equal to a unit vector \mathbf{n}' pointed into the ele-

ment of solid angle $d\Omega'$. Then we have

$$\left(\frac{dW_x}{dp}\right)_{p=1} = \frac{1}{\pi^2 \alpha r_s} \int \frac{d\Omega'}{(\mathbf{n}' - \mathbf{n})^2} \mathbf{n} \cdot \mathbf{n}' = \frac{2}{\pi \alpha r_s} \int_{-1}^1 \frac{x dx}{2(1-x)}. \quad (14)$$

We have put $x = \mathbf{n} \cdot \mathbf{n}'$. Note that the result is indeed logarithmically divergent.

We have treated $(dW_x/dp)_{p=1}$ without approximation. In the higher terms, however, we keep only the leading divergence. Now in differentiating formula (7) for $W_a^{(2)}$, we keep the leading divergence if we differentiate with respect to p only the limits of integration on \mathbf{q} : " $|\mathbf{p} + \mathbf{q}| > 1$ " and " $|\mathbf{p} - \mathbf{q}| < 1$." We find, in fact,

$$\left(\frac{dW_a^{(2)}}{dp}\right)_{p=1} \approx -\frac{2}{\pi^4} \int_{p_2 < 1} d^3 p_2 \int_{|\mathbf{p}_2 + \mathbf{q}| > 1} \frac{d^3 q}{q^4} \times \frac{1}{q^2 + \mathbf{q} \cdot (\mathbf{n} + \mathbf{p}_2)} \delta(1 - |\mathbf{n} + \mathbf{q}|) \mathbf{n} \cdot (\mathbf{n} + \mathbf{q}), \quad (15)$$

where the factor of two comes from the existence of two terms in (7), which make equal contributions to (15). As before, we put $\mathbf{n} + \mathbf{q} = \mathbf{n}'$ and obtain

$$\left(\frac{dW_a^{(2)}}{dp}\right)_{p=1} \approx -\frac{2}{\pi^4} \int \frac{d\Omega'}{[(\mathbf{n}' - \mathbf{n})^2]^2} \times \mathbf{n} \cdot \mathbf{n}' \int_{\substack{p_2 < 1 \\ |\mathbf{n}' - \mathbf{n} + \mathbf{p}_2| > 1}} \frac{d^3 p_2}{(\mathbf{n}' - \mathbf{n}) \cdot (\mathbf{n}' + \mathbf{p}_2)}. \quad (16)$$

We are still interested only in the leading divergence at $\mathbf{n}' = \mathbf{n}$ and so we may take the limit $\mathbf{n}' - \mathbf{n} \rightarrow 0$ in the integral over \mathbf{p}_2 . The limit is 2π . Thus we have

$$\left(\frac{dW_a^{(2)}}{dp}\right)_{p=1} \approx -\frac{8}{\pi^2} \int_{-1}^1 \frac{x dx}{[2(1-x)]^2}. \quad (17)$$

Adding together the terms calculated so far in (3), (14), and (17), we have

$$\left(\frac{dW}{dp}\right)_{p=1} = \frac{2}{\alpha^2 r_s^2} + \frac{2}{\pi \alpha r_s} \int_{-1}^1 \frac{x dx}{2(1-x)} \times \left\{ 1 - \frac{4\alpha r_s}{\pi} \frac{1}{2(1-x)} + \dots \right\}. \quad (18)$$

To complete this series to the desired accuracy, we must look at formula (I-19) for $\epsilon^{(n)}$ and use it to calculate $W^{(n)}$ for $n > 2$. If we do that and compute the leading divergence in $(dW^{(n)}/dp)_{p=1}$, we find that the series in (18) becomes simply a geometric series. We have, thus, with sufficient accuracy to obtain exact values of B

⁴ J. Bardeen, Phys. Rev. **50**, 1098 (1936). That the divergences would disappear in a correct calculation was pointed out by E. P. Wigner, Trans. Faraday Soc. **34**, 678 (1938).

and D in Eq. (11), the result:

$$\left(\frac{dW}{dp}\right)_{p=1} \approx \frac{2}{\alpha^2 r_s^2} + \frac{2}{\pi \alpha r_s} \int_{-1}^1 \frac{x dx}{2(1-x)} \times \left[1 + \frac{4\alpha r_s}{\pi} \frac{1}{2(1-x)} \right]^{-1}. \quad (19)$$

or

$$\left(\frac{dW}{dp}\right)_{p=1} = \frac{2}{\alpha^2 r_s^2} + \frac{1}{\pi \alpha r_s} \{ \ln(\pi/\alpha r_s) - 2 \} + \dots \quad (20)$$

At low temperature, then, the specific heat of a free electron gas is modified through Coulomb interactions by the factor

$$C/C_F = \left[1 + \frac{\alpha r_s}{2\pi} [-\ln r_s + \ln(\pi/\alpha) - 2] + \dots \right]^{-1}, \quad (21)$$

where the expansion is valid at high densities. Inserting numerical values, we have

$$C/C_F = [1 + 0.083 r_s (-\ln r_s - 0.203) + \dots]^{-1}. \quad (22)$$

This is to be compared with the approximate result of Pines,² who finds

$$C/C_F = [1 + 0.083 r_s (-\ln r_s + 1.47) + \dots]^{-1}. \quad (23)$$

The method given here permits the computation of higher terms in the series, and the next correction is now being calculated. Applications to the specific heats of metals are also being studied.

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Correlation Energy of an Electron Gas at High Density

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The correlation energy of an electron gas at high density is evaluated up to terms of orders $(r_s)^0$ and $\log r_s$. It is shown that the correlation energy to this order can be evaluated without using perturbation treatment. The result obtained coincides with the result of formal summation of apparently divergent series arising from small momentum transfer processes which has been discussed fully by Gell-Mann and Brueckner. The method to treat the small momentum transfer effect exactly is given by following the analogy of processes with well-known treatment of systems with Hamiltonians which are bilinear in creation and annihilation operators such as the neutral scalar pair theory. Some simple interpretations of the correlation energy to this order are also given.

RECENTLY, it was shown by Gell-Mann and Brueckner¹ that the correlation energy of an electron gas at high density can be evaluated exactly to order of the constant term $(r_s)^0$ and the term of $\log r_s$, where r_s is the ratio of the radius of a volume within which one electron exists to the Bohr radius and energy is measured in terms of Rydbergs. (The kinetic energy is $2.21/r_s^2$, and the exchange energy is $-0.916/r_s$ per electron.) Their result was obtained by a selected summation of the formally divergent power series expansion of Rayleigh-Schrödinger perturbation theory. This procedure introduces some uncertainties into the final result; in fact, it can be seen that the constant term in the energy contains very curious divergences when the sum is taken in a straightforward manner. Regarding these terms as unphysical, the aforementioned authors discarded them and were able to obtain a unique result.

The simple structure of the diagrams summed by G-B. suggests that it may be possible to find a more rigorous way to get their answer without using a perturbation procedure. In Fig. 1 we give a typical diagram which contributes to the terms of order $(r_s)^0$ and $\ln r_s$. Formally, only the second-order iterated Coulomb

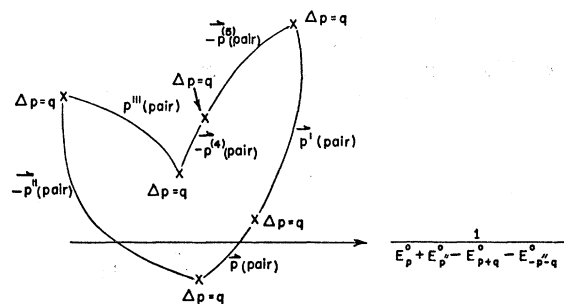


FIG. 1. Typical diagram of a process contributing to the correlation energy terms of order $(r_s)^0$ and $\ln r_s$.

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¹ M. Gell-Mann and K. A. Brueckner, this issue Phys. Rev. 106, 364 (1957), hereafter referred to as G-B.