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EXCHANGE INTEGRAL AND SPECIFIC HEAT OF THE ELECTRON GAS

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Synopsis

A simple expression is derived for the exchange term of the electron gas at any temperature T. For $T \to 0$ we get for the specific heat: $C_v \sim T \ln T + \mathcal{O}(T)$. Using a screened potential, the result can be corrected to: $C_v \sim T |\ln T| + \mathcal{O}(T)$.

The system of an electron gas with positive background has been thoroughly investigated by many authors[1]).

Usually the ground state or high-temperature properties were evaluated, neglecting the wide intermediate region of finite temperatures. The first-order correction due to Coulomb interaction comes from the exchange term. Recently there has been an increased interest in the evaluation of the exchange term for finite temperatures[2,3]). These and previous works[4,5]) deal mainly with an expansion near $T = 0$. Even so the different works disagree as to the behaviour of the specific heat as $T \to 0$.

In the present work a simple expression for the exchange term at any temperature is derived and the implications on the specific heat at $T \to 0$ are studied.

Let $\Omega_1 (z, V, T)$ be the exchange contribution to the thermodynamic potential $\Omega (z, V, T) = -PV$, where z is the fugacity of the system in volume V and pressure P. In the configuration space we have:

$$\Omega_1 (z, V, T) = - \iint \mathrm{d}^3\boldsymbol{r}\, \mathrm{d}^3\boldsymbol{r}' \, \frac{e^2}{|\boldsymbol{r} - \boldsymbol{r}'|} \, |G(\boldsymbol{r} - \boldsymbol{r}')|^2, \tag{1}$$

$$G(\boldsymbol{x}) = \int \frac{\mathrm{d}^3p}{(2\pi)^3} \, n_p \, \mathrm{e}^{-\mathrm{i}\boldsymbol{p}\cdot\boldsymbol{x}} = \frac{1}{2\pi^2 x} \int_0^\infty n_p p \sin px \, \mathrm{d}p, \tag{2}$$

where $n_p = (z^{-1}e^{\beta p^2/2m} + 1)^{-1}$, $\beta = 1/kT$, $P = |\boldsymbol{p}|$, $x = |\boldsymbol{x}|$. $\Omega_1(z, V, T)$ can be more easily recognized if we transform to momentum space:

$$\Omega_1(z, V, T) = -\frac{V}{(2\pi)^6}\iint \mathrm{d}^3p\, \mathrm{d}^3p'\, \frac{4\pi e^2}{(\boldsymbol{p}-\boldsymbol{p}')^2}\, n_p n_{p'} \tag{3}$$

which is the form given in ref. 4. Let us first evaluate the derivative with respect to z. Let us define:

$$g(x) = \int_0^\infty \frac{\cos qx}{z^{-1}e^{\beta q^2/2m} + 1}\, \mathrm{d}q. \tag{4}$$

Then, by using eqs. (1) and (2):

$$\frac{\partial\Omega(z, V, T)}{\partial z} = V\frac{2me^2}{\pi^3\beta z}\int_0^\infty g(x)\,\frac{\mathrm{d}g(x)}{\mathrm{d}x}\,\mathrm{d}x = -V\frac{me^2}{\pi^3\beta z}\, g^2(0). \tag{5}$$

By using the well-known function $f_{3/2}(z)$[6]):

$$f_{3/2}(z) = \frac{4}{\sqrt{\pi}}\int_0^\infty \frac{x^2}{z^{-1}e^{x^2} + 1}\,\mathrm{d}x \tag{6}$$

we obtain:

$$\Omega_1(z, V, T) = -V\frac{2e^2}{\lambda^4}\int_0^z \left[\frac{\partial}{\partial t} f_{3/2}(t)\right]^2 t\,\mathrm{d}t, \tag{7}$$

where $\lambda = (2\pi\beta/m)^{\frac{1}{2}}$.

The lower limit of integration is determined by direct calculation of eq. (1) in the limit $z \to 0$:

$$\lim_{z\to 0}\Omega_1(z, V, T) = -\lim_{z\to 0} V\frac{e^2z^2}{\lambda^4} = 0.$$

(This is the limit where the Boltzmann distribution is valid.)

Eq. (7) gives a simple expression for $\Omega_1(z, V, T)$ as a single integral of a well-known function. The exchange contribution can then be found at any temperature by a simple numerical integration. Evaluation of other thermodynamic quantities can be made with the free energy, which is given up to first order in e^2, by[7]):

$$F(T, V, N) = F_0(T, V, N) + \Omega_1(z_0, V, T), \tag{8}$$

N is the number of particles and z_0 is the interaction free fugacity, which is a function of T, V, N[6]):

$$n = \frac{N}{V} = \frac{2}{\lambda^3} f_{3/2}(z_0). \tag{9}$$

(The factor 2 comes for the spin states.) $F_0(T, V, N)$ is the free energy for fermions with no interaction.

We now proceed to evaluate eq. (7) in the limit of $z_0 \to \infty$, which corresponds to $T \to 0$. We use the expansion[6]):

$$f_{3/2}(z) = \frac{4}{3\sqrt{\pi}} \left[(\ln z)^{3/2} + \frac{\pi^2}{8} (\ln z)^{-\frac{1}{2}} + \mathcal{O}\left((\ln z)^{-5/2}\right) \right]. \tag{10}$$

This is an expansion for large z, and is valid above some z_1. Thus the primitive function of $z\,[\partial f_{3/2}(z)/\partial z]^2$ has the expansion:

$$F(z) = \frac{2}{\pi} \ln^2 z - \frac{\pi}{3} \ln \ln z + \mathcal{O}(\ln z)^{-2}.$$

The integral of eq. (7) up to z_1 is some finite constant, since $f_{3/2}(z)$ is a well-behaved function. Thus we obtain:

$$\int_0^z t \left[\frac{\partial}{\partial t} f_{3/2}(t) \right]^2 \mathrm{d}t = \int_0^{z_1} t \left[\frac{\partial}{\partial t} f_{3/2}(t) \right]^2 \mathrm{d}t + F(z) - F(z_1) = F(z) + \delta,$$

where δ is a constant independent of z:

$$\delta = \int_0^{z_1} t \left[\frac{\partial}{\partial t} f_{3/2}(t) \right]^2 \mathrm{d}t - F(z_1).$$

From eq. (7) we get:

$$\Omega_1(z_0, V, T) = -V \frac{2e^2}{\lambda^4} \left[\frac{2}{\pi} \ln^2 z_0 - \frac{\pi}{3} \ln \ln z_0 + \delta + \mathcal{O}\left(\frac{1}{\ln z_0} \right) \right]. \tag{11}$$

Using eqs. (9) and (10) we have:

$$\ln z_0 = \frac{\varepsilon_F}{kT} \left[1 - \frac{\pi^2}{12} \left(\frac{kT}{\varepsilon_F} \right)^2 + \mathcal{O}(T^4) \right], \tag{12}$$

where ε_F is the Fermi energy $\varepsilon_F = (3\pi^2 n)^{2/3}/2m$. Substituting in eq. (11) we obtain:

$$\Omega_1(T, V, N) = -V\frac{e^2m^2}{2\pi^2}\left[\frac{2}{\pi}\varepsilon_F^2 - (kT)^2\left(\frac{\pi}{3} + \frac{\pi}{3}\ln\frac{\varepsilon_F}{kT} - \delta\right) + \mathcal{O}(T^4)\right]. \tag{13}$$

It is now clear that the logarithmic term gives a dominant contribution to the specific heat at $T \to 0$ since:

$$C_v = -T\frac{\partial^2 F(T, V, N)}{\partial T^2} = -V\frac{e^2m^2k^2}{3\pi}T\ln\frac{\varepsilon_F}{kT} + \mathcal{O}(T). \tag{14}$$

Since the existence of such a logarithmic term has been doubted[2]), we repeat the calculation for $T \to 0$ directly from expression (3) (see appendix) and we obtain exactly the form of eq. (14). Other results[2,4,5]) are found in the literature, except for one case[3]), where eq. (14) is implicitly obtained by some lengthy calculations.

However, the calculation of Wohlfarth[5]), which is quoted in ref. 4, does not correspond exactly to what we are calculating. Wohlfarth obtains $C_v \sim T/\ln T$, by using an inclined step function as the distribution function n_p, with parameters α, β to be determined by the total number of particles and by minimizing the free energy: $(\partial F/\partial \alpha)_T = 0$. This condition determines the distribution function in terms of e^2 self-consistently, and should therefore correspond to summation of some higher-order terms in perturbation expansion. But then we do not know if Wohlfarth's trial function for n_p is a reasonable choice. On the other hand, Ω_1 is a well-defined term in perturbation theory, and can therefore be treated independently. Our calculations correspond to such an exact treatment of the exchange term Ω_1.

Eq. (14) poses a few problems. Firstly the assumption that the elementary excitations of a fermion gas at $T \to 0$ behave like fermions. This assumption leads to $C_v \sim T$[8,9]) as $T \to 0$, which is not correct, at least for the exchange term.

The second problem is even more serious. From eq. (14) we see that C_v is negative below some finite temperature. This is unreasonable, and therefore the exchange term must be corrected by other terms which contain a $T\ln T$ factor. Thus the exchange term cannot be dominant, at least for low temperatures.

Such a correction can take place by considering a screened Coulomb potential: $(e^2/|\boldsymbol{r}|)\,e^{-\eta r}$. We are interested in the screening which is due to the temperature increase. Therefore we assume that $\eta = \gamma 2\pi mkT/P_F$, where $P_F = (2m\varepsilon_F)^{\frac{1}{2}}$ and γ is a dimensionless constant. Such a screening factor, $e^{-\eta r}$, was obtained[10]) with $\gamma = 1$ by summation of ring diagrams. In real systems such a screening may occur also from interactions not included in the electron-gas model. Instead of eq. (5) we now obtain:

$$\frac{\partial \Omega_1(z, V, T)}{\partial z} = V \frac{2me^2}{\pi^3 \beta z} \int_0^\infty e^{-\eta x} g(x) \frac{\mathrm{d}g(x)}{\mathrm{d}x} \mathrm{d}x$$

$$= V \frac{2me^2}{\pi^3 \beta z} \left[-\tfrac{1}{2} g^2(0) + \tfrac{1}{2}\eta \int_0^\infty e^{-\eta x} g^2(x) \,\mathrm{d}x \right] \tag{15}$$

The first term is the exchange term without screening. Since $\eta \sim T$ we take in the second term:

$$g_{T=0}(x) = \int_0^{p_F} \cos qx \,\mathrm{d}x = \sin p_F x / x.$$

Therefore $\Delta\Omega_1$, the correction to lowest order in T due to screening, satisfies:

$$\frac{\partial \Delta\Omega_1}{\partial z} = V \frac{me^2}{\pi^3 \beta z} \eta \int_0^\infty e^{-\eta x} \frac{\sin^2 p_F x}{x^2} \mathrm{d}x. \tag{16}$$

After some calculations we obtain:

$$\Delta\Omega_1(z, V, T) = -\gamma^2 \frac{e^2 m^2 k^2 T^2}{\pi} \ln \frac{\varepsilon_F}{kT} + \mathcal{O}(T^2). \tag{17}$$

Therefore we have for the specific heat:

$$C_v = V \frac{2}{\pi} e^2 m^2 k^2 T (\gamma^2 - \tfrac{1}{6}) \ln \frac{\varepsilon_F}{kT} + \mathcal{O}(T). \tag{18}$$

If $\gamma^2 > \frac{1}{6}$ we have $C_v \sim T |\ln T|$ for $T \to 0$, so that C_v remains positive. Only if $\gamma^2 = \frac{1}{6}$, C_v is linear in T. The screened Coulomb potential represents approximately the effect of the higher-order RPA diagrams. However, a more complete derivation of these terms at finite temperature is still needed in order to determine if the term $T \ln T$ indeed exists for the electron-gas system, and with what coefficient.

In conclusion, expression (7) is a useful form for the exchange term. For low temperatures we have shown that the exchange term cannot be dominant. By using a screened potential the exchange term can be corrected and it is possible that $C_v \sim T |\ln T|$ for $T \to 0$.

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APPENDIX

We give a direct calculation of the leading term in T, as $T \to 0$, of the specific heat due to the exchange term.

The change in the occupation function n_p due to increase in temperature is:

$$\Delta n_q = n_q - \theta\,(p_F - |q|) = \frac{\operatorname{sign} x}{e^{\beta\varepsilon_F |x|} + 1} + R,$$

where $x = [q^2 - p_F^2]/p_F^2$. The residue R comes from the difference in the fugacities at $T \neq 0$ and $T = 0$ according to eq. (12). If we substitute R in the following integral its leading terms are of order T^2.

The leading correction to $\Omega_1\,(z, V, T = 0)$ is derived from eq. (3), and after angular integration we get:

$$\Delta\Omega_1 = \frac{e^2 V}{\pi^3} \int_0^\infty k\,\mathrm{d}k \int_0^\infty q\,\mathrm{d}q \ln \left|\frac{k-q}{k+q}\right| n_k\,(T=0)\,\Delta n_q$$

$$= V\frac{e^2 p_F^4}{4\pi^3} \int_{-1}^\infty \frac{\operatorname{sign} x}{e^{\beta\varepsilon_F |x|} + 1} \left[-x \ln \left|\frac{(1+x)^{\frac{1}{2}} - 1}{(1+x)^{\frac{1}{2}} + 1}\right| - 2\,(1+x)^{\frac{1}{2}}\right] \mathrm{d}x.$$

We can expand the logarithmic term around $x = 0$ and obtain:

$$\Delta\Omega_1 = -V\frac{e^2 p_F^4}{2\pi^3} \int_0^\infty \frac{x \ln \frac{1}{4}x}{e^{\beta\varepsilon_F x} + 1}\,\mathrm{d}x + \mathcal{O}(T^2) = V\,\frac{e^2 m^2 k^2 T^2}{6\pi} \ln \frac{\varepsilon_F}{kT} + \mathcal{O}(T^2).$$

Thus the specific heat is given by eq. (14).

The term $\Delta n_q \Delta n_k$, neglected above, gives a contribution of order T^2. To see this explicitely, let us define

$$\Delta\Omega_1' = \frac{e^2 V}{2\pi^3} \int_0^\infty k\,\mathrm{d}k \int_0^\infty q\,\mathrm{d}q \ln \left|\frac{k-q}{k+q}\right| \Delta n_k \Delta n_q$$

$$= \frac{e^2 V p_F^4}{8\pi^3} \int_{-1}^\infty \mathrm{d}x \int_{-1}^\infty \mathrm{d}y \ln \left|\frac{(1+y)^{\frac{1}{2}} - (1+x)^{\frac{1}{2}}}{(1+y)^{\frac{1}{2}} + (1+x)^{\frac{1}{2}}}\right| \frac{\operatorname{sign} x \cdot \operatorname{sign} y}{(e^{\beta\varepsilon_F |x|} + 1)\,(e^{\beta\varepsilon_F |y|} + 1)},$$

where $y = (k^2 - p_F^2)/p_F^2$ and $x = (q^2 - p_F^2)/p_F^2$.

We can expand the logarithm around $x = y = 0$, and extend the integrations to $-\infty$, which involves an error of order $e^{-\beta\varepsilon_F}$. Thus:

$$\Delta\Omega_1' = \frac{e^2 V p_F^4}{8\pi^3} \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \frac{\ln |\frac{1}{4}(y - x) \operatorname{sign} x \cdot \operatorname{sign} y}{(e^{\beta\varepsilon_F |x|} + 1)(e^{\beta\varepsilon_F |y|} + 1)}$$

$$= \frac{1}{(\beta\varepsilon_F)^2} \frac{e^2 V p_F^4}{4\pi^3} \int_0^{\infty} dx \int_0^{\infty} dy \frac{\ln |(y - x)/(y + x)|}{(e^x + 1)(e^y + 1)}.$$

The last integral is a finite constant so that $\Delta\Omega_1'$ is of order T^2.

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