

Notes on the Sommerfeld expansion for Bloch electrons
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1 The density of states. In the following, we indicate with $\varepsilon_{s,\mathbf{k}}$ the eigenvalues of the Bloch Hamiltonian for one-electron states in a given crystal. The wavevector \mathbf{k} is marked explicitly, while the set of quantum numbers s indicates all other quantum numbers, including. e.g., the spin projection, whenever this is a good quantum number.

The density of states (per unit volume) in D spatial dimensions is then defined as

$$g(\varepsilon) \equiv \sum_s \int_{\text{FBZ}} \frac{d^D \mathbf{k}}{(2\pi)^D} \delta(\varepsilon - \varepsilon_{s,\mathbf{k}}) \equiv \sum_s g_s(\varepsilon),$$

where

$$g_s(\varepsilon) \equiv \int_{\text{FBZ}} \frac{d^D \mathbf{k}}{(2\pi)^D} \delta(\varepsilon - \varepsilon_{s,\mathbf{k}})$$

is the density of states of the band labeled by the set of quantum numbers s , and the integrals are extended over the First Brillouin Zone (FBZ) of the given crystal. Degeneracies, whenever present, are taken into account by the explicit summation over s .

2 Thermodynamical properties of metals. A metal is a crystal in which the highest occupied level at zero temperature, ε_F (Fermi level), falls within a set of partially filled bands, so that $g(\varepsilon_F) > 0$. The thermodynamical properties of Bloch electrons in metals are usually described by quantities that can be written as

$$w = \int_{-\infty}^{+\infty} H_w(\varepsilon) f(\varepsilon - \mu) d\varepsilon,$$

where μ is the chemical potential, the function $H_w(\varepsilon)$ characterizes the corresponding thermodynamic quantity, and is assumed to be identically zero below a certain minimum energy ε_{\min} , hereafter taken as the zero on the energy axis, and to grow at most as a power of ε as $\varepsilon \rightarrow +\infty$, and

$$f(z) = \frac{1}{e^{\beta z} + 1}$$

is the Fermi distribution function, with $\beta = (\kappa_B T)^{-1}$.

In the following, we shall calculate the electron density n , for which $H_n(\varepsilon) = g(\varepsilon)$, and the internal energy per unit volume u , for which $H_u(\varepsilon) = \varepsilon g(\varepsilon)$. In both cases, since $g(\varepsilon) \equiv 0$ for $\varepsilon < 0$, the desired property of a vanishing $H_w(\varepsilon)$ for $\varepsilon < 0$ is guaranteed.

The crucial observation is that at low temperature the derivative of the Fermi function

$$-\frac{df}{d\varepsilon}(\varepsilon - \mu) = \beta \frac{e^{\beta(\varepsilon - \mu)}}{[e^{\beta(\varepsilon - \mu)} + 1]^2}$$

is narrowly peaked at $\varepsilon = \mu$ and behaves as a Dirac δ function, since

$$\int_{-\infty}^{+\infty} \left[-\frac{df}{d\varepsilon}(\varepsilon - \mu) \right] d\varepsilon = 1.$$

Moreover, since it is readily shown that

$$-\frac{df}{d\varepsilon}(\varepsilon - \mu) = \beta f(\varepsilon - \mu)[1 - f(\varepsilon - \mu)] = \beta f(\varepsilon - \mu)f(\mu - \varepsilon),$$

the derivative of the Fermi function is an even function of its argument $\varepsilon - \mu$.

3 The Sommerfeld expansion. Let us define

$$G_w(\varepsilon) \equiv \int_{-\infty}^{\varepsilon} H_w(z) dz$$

as the primitive of $H_w(\varepsilon)$ that vanishes at $-\infty$. Then, upon integration by parts, taking advantage of the fact that $G_w(\varepsilon) f(\varepsilon - \mu)$ vanishes as $\varepsilon \rightarrow \pm\infty$, we find

$$w = \int_{-\infty}^{+\infty} f(\varepsilon - \mu) dG_w(\varepsilon) = \int_{-\infty}^{+\infty} G_w(\varepsilon) \left[-\frac{df}{d\varepsilon}(\varepsilon - \mu) \right] d\varepsilon.$$

Now, taking into account that at low temperatures the quantity in square brackets is narrowly peaked at $\varepsilon = \mu$, it seems a good idea to expand $G_w(\varepsilon)$ in power series around $\varepsilon = \mu$,

$$G_w(\varepsilon) = \sum_{\ell=0}^{\infty} \frac{1}{\ell!} G_w^{(\ell)}(\mu) (\varepsilon - \mu)^\ell,$$

where $G_w^{(\ell)}(\mu)$ is the ℓ -th derivative of G_w calculated at $\varepsilon = \mu$, so that

$$w = \sum_{\ell=0}^{\infty} \frac{1}{\ell!} G_w^{(\ell)}(\mu) \int_{-\infty}^{+\infty} (\varepsilon - \mu)^\ell \left[-\frac{df}{d\varepsilon}(\varepsilon - \mu) \right] d\varepsilon.$$

Since we have remarked that the quantity in square brackets is an even function of its argument, the odd powers disappear and

$$w = \sum_{k=0}^{\infty} \frac{1}{(2k)!} G_w^{(2k)}(\mu) \int_{-\infty}^{+\infty} (\varepsilon - \mu)^{2k} \left[-\frac{df}{d\varepsilon}(\varepsilon - \mu) \right] d\varepsilon.$$

Now, the integrals

$$\frac{1}{(2k)!} \int_{-\infty}^{+\infty} (\varepsilon - \mu)^{2k} \left[-\frac{df}{d\varepsilon}(\varepsilon - \mu) \right] d\varepsilon = \frac{\beta}{(2k)!} \int_{-\infty}^{+\infty} (\varepsilon - \mu)^{2k} \frac{e^{\beta(\varepsilon - \mu)}}{[e^{\beta(\varepsilon - \mu)} + 1]^2} d\varepsilon,$$

under the change of variable $z = \beta(\varepsilon - \mu)$, can be cast in the form

$$\frac{\beta^{-2k}}{(2k)!} \int_{-\infty}^{+\infty} z^{2k} \frac{e^z}{(e^z + 1)^2} dz \equiv a_k (\kappa_B T)^{2k}$$

with

$$a_k \equiv \frac{1}{(2k)!} \int_{-\infty}^{+\infty} z^{2k} \frac{e^z}{[e^z + 1]^2} dz.$$

Gathering all the results, we find

$$w = \sum_{k=0}^{\infty} a_k G_w^{(2k)}(\mu) (\kappa_B T)^{2k}$$

(Sommerfeld expansion), that casts the thermodynamic quantity w in the form of a low-temperature expansion. As we shall argue in the following, when written in terms of dimensionless quantities, the Sommerfeld expansion is an expansion in even powers of $\kappa_B T/\varepsilon_F$. Usually, in metals, the Fermi energy is of the order of 1 eV, that corresponds to a temperature of 1.1×10^4 K. Therefore, even at room temperature, $T = 300$ K, electrons in metals are in a highly degenerate (low-temperature) quantum state, and only the first terms in the expansion need to be taken into account.

For all further developments, one has to consider that $a_0 = 1$, $a_1 = \frac{\pi^2}{6}$, $a_2 = \frac{7\pi^4}{360}$, ..., and $G_w^{(0)}(\mu) = G_w(\mu) = \int_{-\infty}^{\mu} H_w(\varepsilon) d\varepsilon$, $G_w^{(2k)}(\mu) = H_w^{(2k-1)}(\mu)$ for $k \geq 1$, so that

$$w = \int_{-\infty}^{\mu} H_w(\varepsilon) d\varepsilon + \sum_{k=1}^{\infty} a_k H_w^{(2k-1)}(\mu) (\kappa_B T)^{2k}.$$

4 Electron density. To calculate the electron density n , we have to consider that $H_n(\varepsilon) = g(\varepsilon)$. Stopping the Sommerfeld expansion at the term $k = 1$ yields

$$n \approx \int_{-\infty}^{\mu} g(\varepsilon) d\varepsilon + \frac{a_1}{2} g'(\mu) (\kappa_B T)^2.$$

In this expression, the temperature dependence is not made fully explicit, since the chemical potential μ depends on the temperature. To make all the temperature dependence explicit, we proceed as follows. At $T = 0$, we have $\mu(T = 0) = \varepsilon_F$, so we expect small corrections at finite temperatures, and we assume that these corrections are quadratic, $\mu \approx \varepsilon_F + \alpha(\kappa_B T)^2$, checking our assumption *a posteriori*, when determining the value of the unknown coefficient α . Since the second term in the expression for n is already of order $(\kappa_B T)^2$, we can take $g'(\mu) = g'(\varepsilon_F)$, making an error which is of higher order. Furthermore, for small $\mu - \varepsilon_F$,

$$\int_{-\infty}^{\mu} g(\varepsilon) d\varepsilon = \int_{-\infty}^{\varepsilon_F} g(\varepsilon) d\varepsilon + \int_{\varepsilon_F}^{\mu} g(\varepsilon) d\varepsilon \approx \int_{-\infty}^{\varepsilon_F} g(\varepsilon) d\varepsilon + g(\varepsilon_F)(\mu - \varepsilon_F).$$

The first term is nothing but the electron density n calculated at $T = 0$, and the second term reads $g(\varepsilon_F) \alpha(\kappa_B T)^2$. Since n does not depend on the temperature, we find

$$n \approx n + \left[\alpha g(\varepsilon_F) + \frac{\pi^2}{6} g'(\varepsilon_F) \right] (\kappa_B T)^2.$$

Thus, we deduce that the term in square brackets must vanish, up to order $(\kappa_B T)^2$, whence

$$\alpha \approx -\frac{\pi^2}{6} \frac{g'(\varepsilon_F)}{g(\varepsilon_F)},$$

and

$$\mu \approx \varepsilon_F \left[1 - \frac{\pi^2}{6} \frac{g'(\varepsilon_F)}{\varepsilon_F g(\varepsilon_F)} (\kappa_B T)^2 \right].$$

The correction to the chemical potential has a sign opposite to the sign of $g'(\varepsilon_F)$. This is quite obvious, since the Fermi function is symmetric around the point $\varepsilon = \mu$, where it equals $\frac{1}{2}$ at all $T > 0$. Therefore, were it for the distribution alone, the number of electrons that are lost from states below ε_F due to thermal excitation would be exactly equal to the number that is gained above ε_F . But if $g'(\varepsilon_F) > 0$ the states are denser above ε_F than below it, so there would be a neat increase in the number of electrons. Since these cannot be created from nothing, the chemical potential must be diminished by the right amount to compensate for this increase. A similar reasoning explains why μ must increase if $g'(\varepsilon_F) < 0$.

An estimate by order of magnitude gives $|g'(\varepsilon_F)| \sim g(\varepsilon_F)/\varepsilon_F$, therefore an estimate of the relative correction to the chemical potential is

$$\left| \frac{\delta\mu}{\mu} \right| \sim \left(\frac{\kappa_B T}{\varepsilon_F} \right)^2,$$

which is usually a very small number even at room temperature.

To make a comparison, we notice that in the three-dimensional Fermi gas

$$g(\varepsilon) = \frac{3}{2} \frac{n}{\varepsilon_F} \left(\frac{\varepsilon}{\varepsilon_F} \right)^{1/2}, \quad g'(\varepsilon) = \frac{3}{4} \frac{n}{\varepsilon_F} \frac{1}{(\varepsilon_F \varepsilon)^{1/2}}, \quad \text{whence} \quad g(\varepsilon_F) = \frac{3}{2} \frac{n}{\varepsilon_F} = 2\varepsilon_F g'(\varepsilon_F),$$

i.e., $g'(\varepsilon_F) = g(\varepsilon_F)/(2\varepsilon_F)$, which is fully consistent with the estimate of the order of magnitude given above, up to a factor $\frac{1}{2}$. Then

$$\mu \approx \varepsilon_F \left[1 - \frac{\pi^2}{12} \left(\frac{\kappa_B T}{\varepsilon_F} \right)^2 \right],$$

where the correction is always negative, because in the three-dimensional Fermi gas $g'(\varepsilon_F) > 0$.

5 Internal energy. To calculate the electron internal energy per unit volume u , we have to consider that $H_u(\varepsilon) = \varepsilon g(\varepsilon)$. Stopping again the Sommerfeld expansion at the term $k = 1$ yields

$$u \approx \int_{-\infty}^{\mu} \varepsilon g(\varepsilon) d\varepsilon + \frac{\pi^2}{6} [\mu g'(\mu) + g(\mu)] (\kappa_B T)^2,$$

where again part of the temperature dependence is implicit in μ . However, since the correction to μ has been calculated, we can now plug it in, while letting $\mu g'(\mu) + g(\mu) \approx \varepsilon_F g'(\varepsilon_F) + g(\varepsilon_F)$ in front of the explicit $(\kappa_B T)^2$ factor. Then, for small $\mu - \varepsilon_F$,

$$\begin{aligned} u &\approx \int_{-\infty}^{\varepsilon_F} \varepsilon g(\varepsilon) d\varepsilon + \int_{\varepsilon_F}^{\mu} \varepsilon g(\varepsilon) d\varepsilon + \frac{\pi^2}{6} [\varepsilon_F g'(\varepsilon_F) + g(\varepsilon_F)] (\kappa_B T)^2 \\ &\approx u_0 + \varepsilon_F g(\varepsilon_F) \alpha (\kappa_B T)^2 + \frac{\pi^2}{6} [\varepsilon_F g'(\varepsilon_F) + g(\varepsilon_F)] (\kappa_B T)^2, \end{aligned}$$

where u_0 is the value at $T = 0$. Plugging in the expression for α obtained above, we find the final result

$$u \approx u_0 + \frac{\pi^2}{6} g(\varepsilon_F) (\kappa_B T)^2,$$

where now all the temperature dependence is explicit. As an estimate by order of magnitude, $g(\varepsilon_F) \sim u_0/\varepsilon_F^2$ so that again the relative correction is small,

$$\frac{\delta u}{u} \sim \left(\frac{\kappa_B T}{\varepsilon_F} \right)^2.$$

In the three-dimensional Fermi gas, $u_0 = \frac{3}{5} \varepsilon_F n$, hence $g(\varepsilon_F) = \frac{5}{2} \frac{u_0}{\varepsilon_F^2}$, consistent with the above estimate, up to a factor $\frac{5}{2}$. Thus, for the three-dimensional Fermi gas

$$u \approx u_0 \left[1 + \frac{5\pi^2}{12} \left(\frac{\kappa_B T}{\varepsilon_F} \right)^2 \right].$$

6 The specific heat. The specific heat of the electrons is readily calculated as

$$c_V^{el} = \frac{du}{dT} \approx \frac{\pi^2}{3} g(\varepsilon_F) \kappa_B^2 T,$$

and depends on the density of states at the Fermi energy, which is a consequence of the fact that only electrons close to the Fermi level can be thermally excited. The coefficient $\gamma = \frac{\pi^2}{3} g(\varepsilon_F) \kappa_B^2$ is usually introduced to write $c_V^{el} = \gamma T$.

In the Fermi gas $g(\varepsilon_F) = \frac{3n}{2\varepsilon_F}$, hence

$$c_V^{el} \approx \frac{\pi^2}{2} n \kappa_B \left(\frac{\kappa_B T}{\varepsilon_F} \right).$$

The linearity of the specific heat shows that even at room temperature there is no such thing as equipartition for electrons, rather, the estimate given by equipartition ($\frac{3}{2} n \kappa_B$) is suppressed by the small factor $\frac{\kappa_B T}{\varepsilon_F}$.

In a metal, besides the electron contribution, the low-temperature specific heat has also a phonon contribution, therefore

$$c_V = c_V^{el} + c_V^{ph} = \gamma T + A T^3.$$

Then, plotting the measured quantities

$$\frac{c_V}{T} = \gamma + A T^2$$

as a function of T^2 , the intercept gives the electron contribution and the slope gives the phonon contribution.

7 Concluding remarks. The Sommerfeld expansion is a very powerful method to calculate the thermodynamical properties of Bloch electrons in most cases. There are, however, cases in which it is apt to fail. The criterion for failure is that the corrections to the $T = 0$ properties, that are assumedly small, turn out not to be small. This is for instance the case when ε_F is located near a van Hove singularity in the electron spectrum, where the density of states diverges.