Specific heat of electrons in metals

Use $c = T\partial s/\partial T$, where s is the entropy per unit volume. Start from

$$s = -k_B \int g(E)\,(f \ln f + (1-f)\ln(1-f))\,dE$$

where $g(E)$ is the density of levels and f is the Fermi function

$$f(x) = \frac{1}{e^x + 1} \qquad \text{with} \quad x = \frac{E-\mu}{k_B T}$$

Note in passing that s vanishes for $T \to 0$, as it should, because f is either 0 or 1 in that limit. All the specific heats are the same to leading order in T; it is easiest to compute the specific heat at constant μ and V. Then we need

$$\left(\frac{\partial s}{\partial T}\right)_\mu = -k_B \int g(E) \ln\left(\frac{f}{1-f}\right)\frac{\partial f}{\partial T}\,dE$$

Use $\frac{f}{1-f} = e^{-x}$ and $\frac{\partial f}{\partial T} = \frac{\partial f}{\partial x}\frac{\partial x}{\partial T} = -\frac{\partial f}{\partial x}\frac{x}{T}$ to obtain

$$\left(\frac{\partial s}{\partial T}\right)_\mu = -k_B \int g(E)\,x^2\,\frac{\partial f}{\partial x}\frac{dE}{T} \tag{1}$$

This formula is still exact. Now note that

$$-\frac{\partial f}{\partial x} = \frac{e^{-x}}{(e^{-x}+1)^2}$$

is strongly peaked at $E = \mu$ when $k_B T \ll \mu$. Then, in this limit,

$$\frac{\partial s}{\partial T} \simeq k_B^2\, g(\mu) \int_{-\infty}^{\infty} \frac{x^2 e^{-x}\,dx}{(e^{-x}+1)^2}\,dx$$

The exact value of the integral is $\pi^2/3$. At low T, one can replace $g(\mu)$ with $g(E_F)$, where E_F is the value of μ at $T = 0$. Then $c = \gamma T$ (at constant μ) and also $s = \gamma T$, with

$$\gamma = \left(\frac{\pi^2}{3}\right) k_B^2\, g(E_F)$$

For a gas of non-relativistic free electrons in 3d, substitute from AM's eq. (2.65),

$$g(E_F) = \frac{3}{2}\frac{n}{E_F}$$

To get higher order terms from Eq. (1), insert the Taylor series $g(E) = \sum_p g^{(p)}(\mu)(E-\mu)^p/p! = \sum_p (k_B T)^p g^{(p)}(\mu) x^p/p!$ and look up in Arfken and Weber the values of

$$\int_{-\infty}^{\infty} \frac{x^{2+p} e^{-x}\,dx}{(e^{-x}+1)^2} \tag{2}$$

for even p (the odd values of p give 0).