**ETH**

Eidgenössische Technische Hochschule Zürich
Swiss Federal Institute of Technology Zurich

**Solid State Theory**

**Solution 6**

FS 15

PD V. Geshkenbein

## Problem 6.1  Specific Heat of a Semiconductor and Graphene

a) For $k_B T \ll E_g$ only the band edges are important, so we can approximate the energy dispersion as

$$\varepsilon_v(\mathbf{k}) = -\frac{\hbar^2 \mathbf{k}^2}{2m_v}, \tag{1}$$

$$\varepsilon_c(\mathbf{k}) = E_g + \frac{\hbar^2 \mathbf{k}^2}{2m_c}, \tag{2}$$

where $m_{v,c}$ are the effective masses in the two bands. The gap extends for energies $\varepsilon \in (0, E_g)$.

We start again by finding the dependence $\mu(T)$ of chemical potential on temperature. At zero temperature it is in the middle of the gap. For non-zero temperature it shifts. To determine $\mu(T)$ we consider the fixed density of particles, i.e.

$$0 = 2 \int \frac{\mathrm{d}^3\mathbf{k}}{(2\pi)^3} \left[1 - f(\varepsilon_v(\mathbf{k}); \mu(T), T)\right] - 2 \int \frac{\mathrm{d}^3\mathbf{k}}{(2\pi)^3} f(\varepsilon_c(\mathbf{k}); \mu(T), T) \tag{3}$$

$$= 2 \int \frac{\mathrm{d}^3\mathbf{k}}{(2\pi)^3} \frac{1}{\mathrm{e}^{-[\varepsilon_v(\mathbf{k})-\mu(T)]/k_\mathrm{B}T} + 1} - 2 \int \frac{\mathrm{d}^3\mathbf{k}}{(2\pi)^3} \frac{1}{\mathrm{e}^{[\varepsilon_c(\mathbf{k})-\mu(T)]/k_\mathrm{B}T} + 1}. \tag{4}$$

If we assume that $k_\mathrm{B}T \ll \mu$ and $k_\mathrm{B}T \ll E_g - \mu$, then we can neglect the "+1" in the Fermi-Dirac distribution function and the previous equation simplifies to

$$0 = 2 \int \frac{\mathrm{d}^3\mathbf{k}}{(2\pi)^3} \mathrm{e}^{[\varepsilon_v(\mathbf{k})-\mu(T)]/k_\mathrm{B}T} - 2 \int \frac{\mathrm{d}^3\mathbf{k}}{(2\pi)^3} \mathrm{e}^{-[\varepsilon_c(\mathbf{k})-\mu(T)]/k_\mathrm{B}T}. \tag{5}$$

Note that this corresponds to using Maxwell-Boltzmann statistics as for the ideal gas, rather than the Fermi-Dirac statistics.

To proceed, we define the density of states in the valence and conduction bands. For an isotropic dispersion $\varepsilon_\mathbf{k} = \varepsilon_k$ we have

$$D(\varepsilon) = \frac{2}{V} \sum_\mathbf{k} \delta(\varepsilon - \varepsilon_\mathbf{k}) = \frac{2}{(2\pi)^3} \int \mathrm{d}^3\mathbf{k}\, \delta(\varepsilon - \varepsilon_\mathbf{k}) \tag{6}$$

$$= \frac{8\pi}{(2\pi)^3} \int \mathrm{d}k\, k^2\, \delta(\varepsilon - \varepsilon_k) = \frac{1}{\pi^2} \frac{k_\varepsilon^2}{\left|\frac{\partial \varepsilon_k}{\partial k}\right|_{k=k_\varepsilon}}, \tag{7}$$

where we first went from a summation to an integral by approximating $\frac{1}{V}\sum_\mathbf{k} \approx \frac{1}{(2\pi)^3}\int \mathrm{d}^3\mathbf{k}$, then transformed the integral to spherical coordinates, and finally used that

$$\int \mathrm{d}x f(x)\, \delta(g(x)) = \sum_{x_0} \frac{f(x_0)}{|g'(x_0)|}, \tag{8}$$

where $x_0$ are the roots of $g(x)$ and the prime indicates the first derivative.

Plugging the dispersions (1) and (2) into (7), we find specifically

$$D_v(\varepsilon) = \frac{1}{2\pi^2} \left(\frac{2m_v}{\hbar^2}\right)^{\frac{3}{2}} \sqrt{-\varepsilon} \tag{9}$$

$$D_c(\varepsilon) = \frac{1}{2\pi^2} \left(\frac{2m_v}{\hbar^2}\right)^{\frac{3}{2}} \sqrt{\varepsilon - E_g}. \tag{10}$$

With these we can change integration over momenta to integration over energies. With the help of integral

$$\int_0^\infty \sqrt{x}\,\mathrm{e}^{-\frac{x}{k_B T}} = \frac{\sqrt{\pi}}{2}(k_B T)^{\frac{3}{2}} \tag{11}$$

we easily find

$$
\begin{aligned}
0 &= \int_{-\infty}^0 \mathrm{d}\varepsilon\, D_v(\varepsilon)\mathrm{e}^{[\varepsilon-\mu(T)]/k_B T} - \int_{E_g}^{+\infty} \mathrm{d}\varepsilon\, D_c(\varepsilon)\mathrm{e}^{-[\varepsilon-\mu(T)]/k_B T} \tag{12}\\
&= \left(\frac{1}{2\pi^2\hbar^3}\right)\left\{ (2m_v)^{\frac{3}{2}}\mathrm{e}^{-\frac{\mu(T)}{k_B T}}\int_{-\infty}^0 \mathrm{d}\varepsilon\sqrt{-\varepsilon}\,\mathrm{e}^{\frac{\varepsilon}{k_B T}} - (2m_c)^{\frac{3}{2}}\mathrm{e}^{\frac{(\mu(T)-E_g)}{k_B T}}\int_0^\infty \mathrm{d}\varepsilon\sqrt{\varepsilon}\,\mathrm{e}^{\frac{\varepsilon}{k_B T}} \right\} \\
&= \left(\frac{1}{2\pi^2\hbar^3}\right)\frac{\sqrt{\pi}}{2}(k_B T)^{\frac{3}{2}}\left\{ (2m_v)^{\frac{3}{2}}\mathrm{e}^{-\frac{\mu(T)}{k_B T}} - (2m_c)^{\frac{3}{2}}\mathrm{e}^{\frac{(\mu(T)-E_g)}{k_B T}} \right\}. \tag{13}
\end{aligned}
$$

From this it follows that

$$\mu(T) = \frac{E_g}{2} + \frac{3}{4}k_B T\log\left(\frac{m_v}{m_c}\right). \tag{14}$$

With the above results we can simplify the distribution function of electrons in the conductance band as

$$
\begin{aligned}
f_e(\varepsilon_c(\mathbf{k})) &\approx \mathrm{e}^{-[E_g+\frac{\hbar^2\mathbf{k}^2}{2m_c}-\mu(T)]/k_B T} = \mathrm{e}^{-\frac{\hbar^2\mathbf{k}^2}{2m_c k_B T}}\mathrm{e}^{-\frac{E_g}{2k_B T}}\mathrm{e}^{\frac{3}{4}\log\left(\frac{m_v}{m_c}\right)} \tag{15}\\
&= \mathrm{e}^{-\frac{\hbar^2\mathbf{k}^2}{2m_c k_B T}}\mathrm{e}^{-\frac{E_g}{2k_B T}}\left(\frac{m_v}{m_c}\right)^{\frac{3}{4}} \tag{16}
\end{aligned}
$$

and for the holes in the valence band similarly as

$$f_h(\varepsilon_v(\mathbf{k})) \approx \mathrm{e}^{-\frac{\hbar^2\mathbf{k}^2}{2m_c k_B T}}\mathrm{e}^{-\frac{E_g}{2k_B T}}\left(\frac{m_c}{m_v}\right)^{\frac{3}{4}}. \tag{17}$$

It will later be useful to know the number of electrons (which is equal to the number of holes) excited at temperature $T$

$$
\begin{aligned}
n_e(T)\,(=n_h(T)) &= \int\frac{\mathrm{d}^3\mathbf{k}}{4\pi^3}\mathrm{e}^{-\frac{(\varepsilon_c-\mu)}{k_B T}} \tag{18}\\
&= \int\frac{\mathrm{d}^3\mathbf{k}}{4\pi^3}\mathrm{e}^{-\frac{\hbar^2\mathbf{k}^2}{2m_c k_B T}}\mathrm{e}^{-\frac{E_g}{2k_B T}}\left(\frac{m_v}{m_c}\right)^{\frac{3}{4}} \tag{19}\\
&= \frac{1}{\pi^2}\int_0^\infty k^2\mathrm{d}k\,\mathrm{e}^{-\frac{\hbar^2 k^2}{2m_c k_B T}}\mathrm{e}^{-\frac{E_g}{2k_B T}}\left(\frac{m_v}{m_c}\right)^{\frac{3}{4}} \tag{20}\\
&= \frac{1}{\sqrt{2}}\mathrm{e}^{-\frac{E_g}{2k_B T}}\left(\frac{k_B T}{\pi\hbar^2}\right)^{3/2}(m_v m_c)^{3/4} \tag{21}
\end{aligned}
$$

where in the second step we wend to spherical coordinates and in the last step we performed Gaussian integration

$$\int_0^\infty \mathrm{d}x\,x^2\mathrm{e}^{-ax^2} = \frac{\sqrt{\pi}}{4a^{\frac{3}{2}}}. \tag{22}$$

We finally find the energy of the system at finite temperature. Energy of the electrons in conduction band (per unit volume) is

$$
\begin{aligned}
u_e(T) &= \frac{1}{\pi^2} \int_0^\infty k^2 \mathrm{d}k \, \varepsilon_c(k) f_e(\varepsilon_c(k)) && (23) \\
&= \frac{1}{\pi^2} \int_0^\infty k^2 \mathrm{d}k \left( E_g + \frac{\hbar^2 k^2}{2m_c} \right) \mathrm{e}^{-\frac{\hbar^2 \mathbf{k}^2}{2m_c k_{\mathrm B} T}} \mathrm{e}^{-\frac{E_g}{2k_{\mathrm B} T}} \left( \frac{m_v}{m_c} \right)^{\frac{3}{4}} && (24) \\
&\overset{(21)}{=} E_g n_e(T) + \frac{3}{2\sqrt{2}} k_{\mathrm B} T \left( \frac{k_{\mathrm B} T}{\pi \hbar^2} \right)^{\frac{3}{2}} \mathrm{e}^{-\frac{E_g}{2k_{\mathrm B} T}} (m_c m_v)^{3/4} && (25) \\
&\overset{(21)}{=} \left[ E_g + \frac{3}{2} k_{\mathrm B} T \right] n_e(T) && (26)
\end{aligned}
$$

where in the third line we used (22) and

$$
\int_0^\infty \mathrm{d}x \, x^4 \mathrm{e}^{-ax^2} = \frac{3\sqrt{\pi}}{8 a^{\frac{5}{2}}}. \tag{27}
$$

The energy of the holes in the valence band is

$$
u_h(T) = \frac{1}{\pi^2} \int_0^\infty k^2 \mathrm{d}k \, (-\varepsilon_c(k)) f_e(\varepsilon_c(k)). \tag{28}
$$

Its evaluation is completely analogous, the result is

$$
u_h(T) = \frac{3}{2} k_{\mathrm B} T n_h(T). \tag{29}
$$

If we define the total carrier density $n(T) = n_e(T) + n_h(T)$, the total internal energy density is

$$
u(T) = \left[ \frac{3}{2} k_{\mathrm B} T + \frac{E_g}{2} \right] n(T). \tag{30}
$$

Finally, the specific heat is

$$
c_V = \frac{3}{2} n(T) k_{\mathrm B} + \left[ \frac{3}{2} k_{\mathrm B} T + \frac{E_g}{2} \right] \frac{\partial n(T)}{\partial T}. \tag{31}
$$

We see that the specific heat of a semiconductor is given by a contribution similar to the specific heat of an ideal gas of excitations that are already present in the system due to thermal excitation, plus an additional contribution originating from the excitation of new particle hole pairs $\sim \frac{\partial n(T)}{\partial T}$.

It follows from (21) that

$$
\frac{\partial n(T)}{\partial T} = \left( \frac{3}{2} + \frac{E_g}{2 k_{\mathrm B} T} \right) \frac{n(T)}{T}, \tag{32}
$$

so we can rewrite the specific heat as

$$
c_V = \left[ \frac{15}{4} k_{\mathrm B} + \frac{E_g}{T} \left( \frac{3}{2} + \frac{E_g}{4 k_{\mathrm B} T} \right) \right] n(T). \tag{33}
$$

Thus, the part of the specific heat originating from the excitation of additional particles dominates over the ideal gas-like part for small temperatures!

b) We first demonstrate that due to the perfect particle-hole symmetry in graphene $\varepsilon_v(\mathbf{k}) = -\varepsilon_c(\mathbf{k})$, the chemical potential is fixed at $\mu = 0$ at all temperatures. To see this we write

$$n_e = \frac{1}{(2\pi)^2} \int \mathrm{d}^2\mathbf{k} f(\varepsilon_c(\mathbf{k})) = \frac{1}{(2\pi)^2} \int \mathrm{d}^2\mathbf{k} \frac{1}{e^{\beta(\varepsilon_c(\mathbf{k})-\mu)} + 1} \tag{34}$$

$$n_h = \frac{1}{(2\pi)^2} \int \mathrm{d}^2\mathbf{k}[1 - f(-\varepsilon_c(\mathbf{k}))] = \frac{1}{(2\pi)^2} \int \mathrm{d}^2\mathbf{k} \frac{1}{e^{\beta(\varepsilon_c(\mathbf{k})+\mu)} + 1}. \tag{35}$$

By comparing the previous two lines it is obvious that $n_e = n_h$ if (and only if) $\mu = 0$. This is a great simplification!

For the density of states we have

$$D(\varepsilon) = \frac{2 \cdot 2}{A} \sum_{\vec{k}} \delta(\varepsilon - \varepsilon_{\vec{k}}) \tag{36}$$

where the spins lead to a degeneracy of 2 and the two equivalent Dirac points to another degeneracy of 2 (valley degeneracy), and $A$ denotes the area of the graphene sheet.

Due to the symmetry of the band structure it is enough to consider the case $\varepsilon > 0$. Again, we replace the sum by an integral and find

$$D(\varepsilon) = \frac{4}{(2\pi)^2} \int \mathrm{d}^2\mathbf{k}\delta(\varepsilon - \varepsilon_{\vec{k}}) = \frac{2}{\pi} \int_0^\infty k\,\mathrm{d}k\delta(\varepsilon - \hbar v_{\mathrm{F}}k) \tag{37}$$

$$= \frac{2}{\pi\hbar v_{\mathrm{F}}} \int_0^\infty k\,dk\,\delta\left(\frac{\varepsilon}{\hbar v_F} - k\right) = \frac{2}{\pi(\hbar v_{\mathrm{F}})^2}|\varepsilon|, \tag{38}$$

which is linear in the energy.

We are ready to evaluate the internal energy $u$. We find

$$u(T) - u_0 = \int \mathrm{d}\varepsilon\, \varepsilon D(\varepsilon) f(\varepsilon) - u_0 \tag{39}$$

$$= \frac{2}{\pi(\hbar v_{\mathrm{F}})^2} \left(\int_{-\infty}^{+\infty} \mathrm{d}\varepsilon \frac{\varepsilon|\varepsilon|}{e^{\beta(\varepsilon)} + 1} - \int_{-\infty}^0 \mathrm{d}\varepsilon\, \varepsilon|\varepsilon|\right) \tag{40}$$

$$= \frac{2}{\pi(\hbar v_{\mathrm{F}})^2} \left(\int_0^\infty \mathrm{d}\varepsilon \frac{\varepsilon^2}{e^{\beta\varepsilon} + 1} + \int_{-\infty}^0 \mathrm{d}\varepsilon \frac{-\varepsilon^2}{e^{\beta\varepsilon} + 1} + \int_{-\infty}^0 \mathrm{d}\varepsilon\, \varepsilon^2\right) \tag{41}$$

$$= \frac{2}{\pi(\hbar v_{\mathrm{F}})^2} \left(\int_0^\infty \mathrm{d}\varepsilon \frac{\varepsilon^2}{e^{\beta\varepsilon} + 1} + \int_{-\infty}^0 \mathrm{d}\varepsilon \frac{\varepsilon^2}{e^{-\beta\varepsilon} + 1}\right) \tag{42}$$

$$= \frac{4}{\pi(\hbar v_{\mathrm{F}})^2\beta^3} \int_0^\infty \mathrm{d}x \frac{x^2}{e^x + 1} \tag{43}$$

$$= \frac{4(k_{\mathrm{B}}T)^3}{\pi(\hbar v_{\mathrm{F}})^2} \frac{3}{2}\zeta(3). \tag{44}$$

where we used that

$$\int_0^\infty \mathrm{d}k \frac{k^n}{e^k + 1} = \left(1 - \frac{1}{2^n}\right)\Gamma(n+1)\zeta(n+1) \tag{45}$$

for $n > -1$. The specific heat is

$$c_V = \left(\frac{\partial u}{\partial T}\right)_{N,V} = \frac{18\zeta(3)k_{\mathrm{B}}}{\pi(\hbar v_{\mathrm{F}})^2}(k_{\mathrm{B}}T)^2. \tag{46}$$

## Problem 6.2 Spin Susceptibility of a Metal, a Semiconductor, and Graphene

a) An external magnetic field $H$ coupling to the electron spins $s = \pm 1$ (neglecting any orbital effects) changes the energy according to

$$\varepsilon_{\mathbf{k},s} = \varepsilon_{\mathbf{k}} - \mu_{\mathrm{B}} s H, \tag{47}$$

where $\mu_B$ is the Bohr magneton. There are now two distinct Fermi-Dirac distributions and the number of electrons in each spin state is given by

$$n_s(H) = \int \mathrm{d}\varepsilon \frac{1}{2} D(\varepsilon) f(\varepsilon_{\mathbf{k},s}). \tag{48}$$

With the magnetization defined as

$$M = \mu_{\mathrm{B}}(n_+ - n_-), \tag{49}$$

we immediately find

$$M = \mu_{\mathrm{B}} \int \mathrm{d}\varepsilon \frac{1}{2} D(\varepsilon) \left[ f(\varepsilon - \mu_{\mathrm{B}} H) - f(\varepsilon + \mu_{\mathrm{B}} H) \right] \tag{50}$$

$$\approx \mu_{\mathrm{B}}^2 H \int \mathrm{d}\varepsilon D(\varepsilon) \left( -\frac{\partial f}{\partial \varepsilon} \right) \overset{(52)}{\approx} \mu_{\mathrm{B}}^2 H D(\varepsilon_{\mathrm{F}}). \tag{51}$$

In the very last step we used the Sommerfeld expansion (cf. lecture 6)

$$\int_{-\infty}^{\infty} \mathrm{d}\varepsilon \frac{H(\varepsilon)}{\mathrm{e}^{(\varepsilon-\mu)/k_B T} + 1} = \int_{-\infty}^{\mu} \mathrm{d}\varepsilon \ H(\varepsilon) + \sum_{n=1}^{\infty} a_n (k_B T)^{2n} \left. \frac{\mathrm{d}^{2n-1} H(\varepsilon)}{\mathrm{d}\varepsilon^{2n-1}} \right|_{\varepsilon=\mu} \tag{52}$$

where $a_1 = \pi^2/6$, $a_2 = 7\pi^4/360, \ldots$.

The Pauli spin susceptibility is given by

$$\chi_{\mathrm{Pauli}} = \left. \frac{\partial M}{\partial H} \right|_{H=0} = \mu_{\mathrm{B}}^2 D(\varepsilon_{\mathrm{F}}), \tag{53}$$

i.e. in the leading order it is temperature independent.

b) As for the metal, we have

$$M \approx \mu_{\mathrm{B}}^2 H \int \mathrm{d}\varepsilon D(\varepsilon) \left( -\frac{\partial f}{\partial \varepsilon} \right). \tag{54}$$

For the semiconductor, however, we have to be more careful with the derivative because of the gap.

Neglecting excitons and other interactions, we simply model the semiconductor as a paramagnetic ideal gas. Both the electron and the hole system are unpolarized at zero applied field (same number of up and down spins in the thermally excited electrons) and their contribution to the magnetization is the same, $M_{tot} = M_h + M_e$.

Again using the approximation of $\varepsilon \gg k_B T$, we simplify the expression

$$\left( -\frac{\partial f}{\partial \varepsilon} \right) = \frac{\beta \mathrm{e}^{\beta(\varepsilon_c - \mu)}}{(\mathrm{e}^{\beta(\varepsilon_c - \mu)} + 1)^2} \approx \beta \mathrm{e}^{-\beta(\varepsilon_c - \mu)} \tag{55}$$

and we find for the electrons in the conduction band

$$M_e = \mu_{\mathrm{B}}^2 H \beta \int \frac{\mathrm{d}^3 k}{4\pi^3} \mathrm{e}^{-\beta(\varepsilon_c - \mu)}. \tag{56}$$

But this is exactly the integral (18) we had before for the number of electrons. Using $n(T) = n_h(T) + n_e(T)$ we can write immediately

$$M_{\mathrm{tot}} = (M_h + M_e) \approx \mu_{\mathrm{B}}^2 H \beta n(T) \tag{57}$$

which gives

$$\chi_{\mathrm{Pauli}} = \left( \left. \frac{\partial M_{\mathrm{tot}}}{\partial H} \right|_{H=0} \right)_{T,V,N} = \frac{\mu_{\mathrm{B}}^2}{k_{\mathrm{B}}} \frac{n(T)}{T}. \tag{58}$$

This is like Curie's law, reflecting the ideal gas behaviour of the semiconductor. However, the particle density $n(T)$ is temperature dependent and decays exponentially at low temperatures.

As a consequence, the major contribution to the susceptibility in semiconductors stems from the diamagnetism of the ion cores. In doped semiconductors, however, the conduction electron diamagnetism can be dominant.

c) We start again with

$$M \approx \mu_{\mathrm{B}}^2 H \int \mathrm{d}\varepsilon D(\varepsilon) \left( -\frac{\partial f}{\partial \varepsilon} \right). \tag{59}$$

We shall only calculate the contribution from electrons in the conduction band. Due to the perfect particle-hole symmetry the contribution of holes in the valence band will be identical, $M_h = M_e$. We find using the result (38) for the density of states in graphene

$$M_e \approx \mu_{\mathrm{B}}^2 H \frac{2}{\pi(\hbar v_{\mathrm{F}})^2} \int_0^\infty \mathrm{d}\varepsilon\, \varepsilon \frac{\beta \mathrm{e}^{\beta\varepsilon}}{(\mathrm{e}^{\beta\varepsilon} + 1)^2} \tag{60}$$

$$= \mu_{\mathrm{B}}^2 H \frac{2}{\pi(\hbar v_{\mathrm{F}})^2 \beta} \int_0^\infty \mathrm{d}x \frac{x\,\mathrm{e}^x}{(\mathrm{e}^x + 1)^2} \tag{61}$$

$$= \mu_{\mathrm{B}}^2 H \frac{2}{\pi(\hbar v_{\mathrm{F}})^2 \beta} \int_0^\infty \mathrm{d}t \frac{t}{\cosh^2 t} \tag{62}$$

$$= \mu_{\mathrm{B}}^2 H \frac{2}{\pi(\hbar v_{\mathrm{F}})^2 \beta} \log 2. \tag{63}$$

where in the second line we substituted $x = \beta\varepsilon$ and in the third line $t = x/2$. In the last line we used that

$$\int \mathrm{d}t \frac{t}{\cosh^2 t} = -\log[\cosh(t)] + t \tanh t. \tag{64}$$

The total magnetization is twice the result (63) and the Pauli spin susceptibility thus is

$$\chi_{\mathrm{Pauli}} = \mu_{\mathrm{B}}^2 \frac{4 \log 2}{\pi(\hbar v_{\mathrm{F}})^2} k_{\mathrm{B}} T. \tag{65}$$

Note that in real graphene, the susceptibility due to Landau diamagnetism of free electrons and holes is dominant.