

Lecture 17 – Degenerate Fermi gas II (finite temperature)

PREVIOUSLY: In degenerate quantum gases $n > n_Q$, or $T < T_d$, and quantum statistics must be taken into account. Some common fermionic systems, like conduction e^- in metals, are strongly degenerate for any practical range of temperatures ($n \gg n_Q$ since $T \ll T_d \sim 10^5$ K), and their behavior is close to that at $T = 0$ even at room temperature.

Last time we solved

$$N = \int_0^\infty d\varepsilon D(\varepsilon) f_{FD}(\varepsilon, T) \quad U = \int_0^\infty d\varepsilon \varepsilon D(\varepsilon) f_{FD}(\varepsilon, T)$$

at $T = 0$ for a 3-D degenerate Fermi gas to obtain $\varepsilon_F \equiv \mu(0)$ and $U(0)$. $T_F \equiv \varepsilon_F / k_B \approx T_d$ so $T \ll T_F$.

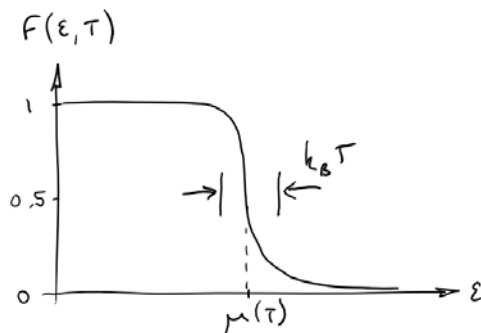
TODAY: We will calculate $\mu(T)$ and $U(T)$ by expanding about small T :

$$\mu(T) = \underbrace{\mu(0)}_{\varepsilon_F} + \mathcal{O}(T^2) \quad U(T) = \underbrace{U(0)}_{\frac{3}{5} N \varepsilon_F} + \mathcal{O}(T^2)$$

We're dealing with integrals of the form:

$$I = \int_0^\infty d\varepsilon \varepsilon^n D(\varepsilon) f(\varepsilon, T) \quad \text{for } n = \begin{cases} 0 & I = N \\ 1 & I = U \end{cases}$$

(Note: we'll drop the "FD" since it's understood). Define $\phi(\varepsilon) \equiv \varepsilon^n D(\varepsilon)$



The Fermi-Dirac distribution $f(\varepsilon, T)$ is very close to a step function for $T \ll T_F$. $f(\varepsilon, T)$ varies rapidly near $\varepsilon = \mu(T)$

On the other hand, $\phi(\varepsilon)$ varies slowly near $\varepsilon = \mu(T)$

We will use this to make approximations

KEY CONCEPT: Sommerfeld expansion

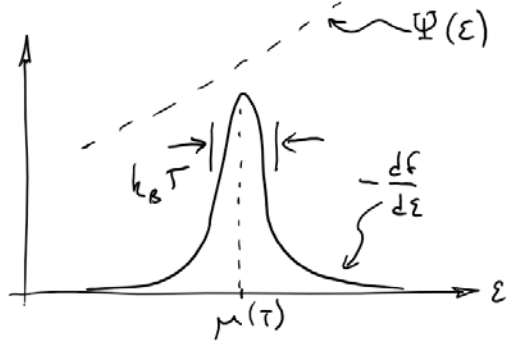
Define $\Psi(\varepsilon) = \int_0^\varepsilon d\varepsilon' \phi(\varepsilon')$ and integrate I by parts

$$I = \int_0^\infty d\varepsilon f(\varepsilon, T) \phi(\varepsilon) = f(\varepsilon, T) \Psi(\varepsilon) \Big|_0^\infty - \int_0^\infty d\varepsilon \frac{df(\varepsilon, T)}{d\varepsilon} \Psi(\varepsilon)$$

$$\begin{array}{ccc} \uparrow & \uparrow & \\ f(\infty, T) = 0 & \Psi(0) = 0 & \end{array}$$

So, we have

$$I = - \int_0^{\infty} d\varepsilon \frac{df(\varepsilon, T)}{d\varepsilon} \Psi(\varepsilon)$$



$-\frac{df(\varepsilon, T)}{d\varepsilon} = \frac{\beta e^{\beta(\varepsilon - \mu)}}{(e^{\beta(\varepsilon - \mu)} + 1)^2}$ is a very sharp function peaked at $\varepsilon = \mu(T)$ and with a width of $\sim k_B T$

On the other hand, $\Psi(\varepsilon)$ varies slowly near $\varepsilon = \mu(T)$

Therefore, we can expand $\Psi(\varepsilon)$ about $\varepsilon = \mu(T)$:

$$\begin{aligned} \Psi(\varepsilon) &= \Psi(\mu) + \Psi'(\mu)(\varepsilon - \mu) + \frac{1}{2}\Psi''(\mu)(\varepsilon - \mu)^2 + \dots \\ &= \sum_{m=0}^{\infty} \frac{1}{m!} \Psi^{(m)}(\mu)(\varepsilon - \mu)^m \end{aligned}$$

and the integral becomes

$$\begin{aligned} I &= - \sum_{m=0}^{\infty} \frac{1}{m!} \Psi^{(m)}(\mu) \int_0^{\infty} d\varepsilon (\varepsilon - \mu)^m \frac{df(\varepsilon, T)}{d\varepsilon} \\ &= + \sum_{m=0}^{\infty} \frac{1}{m!} \Psi^{(m)}(\mu) \int_0^{\infty} d\varepsilon \frac{\beta e^{\beta(\varepsilon - \mu)}}{(e^{\beta(\varepsilon - \mu)} + 1)^2} (\varepsilon - \mu)^m \end{aligned}$$

Let's change variables to $x \equiv \beta(\varepsilon - \mu)$. The integral becomes: $\beta^{-m} \int_{-\beta\mu}^{\infty} dx \frac{x^m e^x}{(e^x + 1)^2}$

Look at lower limit: $\mu \approx \varepsilon_f$ and $T \ll T_f$ so we expect $\beta\mu = \mu / k_B T \gg 1$.

Also, the integrand is negligible for $x \ll 0$, so it's fine to replace the lower limit with $-\infty$

So, we need to evaluate integrals of the form: $I_m \equiv \int_{-\infty}^{\infty} dx \frac{x^m e^x}{(e^x + 1)^2}$

For $m = 0$:
$$I_0 = \int_{-\infty}^{\infty} dx \frac{e^x}{(e^x + 1)^2} = \left. \frac{-1}{e^x + 1} \right|_{-\infty}^{\infty} = 1$$

Question 1: What is the first non-zero order $m > 0$ in the expansion?

$I_m = 0$ for all odd m because the integrands are odd functions of x : $\frac{x^m e^x}{(e^x + 1)^2} = \frac{x^m}{(e^x + 1)(1 + e^{-x})}$

All even m terms are non-zero because the integrands are positive.

So, the next higher order is $m = 2$.

For $m = 2$, evaluating the integral takes a bit more algebra (which is not worth our time):

$$I_2 = \int_{-\infty}^{\infty} dx \frac{x^2 e^x}{(e^x + 1)^2} = 2\zeta(2) = \frac{\pi^2}{3}$$

Putting it all together:

$$I = \int_0^{\infty} d\varepsilon f(\varepsilon, T) \phi(\varepsilon) = \sum_{m \text{ even}} \frac{1}{m!} \Psi^{(m)}(\mu) (k_B T)^m I_m = \Psi(\mu) + \frac{\pi^2}{6} (k_B T)^2 \Psi''(\mu) + \dots$$

Recalling that $\Psi(\varepsilon) = \int_0^{\varepsilon} d\varepsilon' \phi(\varepsilon')$, we get the final form of the Sommerfeld expansion:

$$\int_0^{\infty} d\varepsilon f(\varepsilon, T) \phi(\varepsilon) = \int_0^{\mu} d\varepsilon \phi(\varepsilon) + \frac{\pi^2}{6} (k_B T)^2 \phi'(\mu) + \dots$$

The next term is $\mathcal{O}(T^4)$.

Now consider the integral for N , the number of particles. Since N is fixed, this expression is a constraint that allows us to determine the chemical potential μ

$$N = \int_0^{\infty} d\varepsilon f(\varepsilon, T) D(\varepsilon) = \int_0^{\mu} d\varepsilon D(\varepsilon) + \frac{\pi^2}{6} (k_B T)^2 D'(\mu) + \dots$$

Splitting the first term into two integrals from 0 to ε_F , and from ε_F to μ :

$$N \approx \underbrace{\int_0^{\varepsilon_F} d\varepsilon D(\varepsilon)}_{\mathcal{N}} + \underbrace{\int_{\varepsilon_F}^{\mu} d\varepsilon D(\varepsilon)}_{\approx D(\varepsilon_F)(\mu - \varepsilon_F)} + \frac{\pi^2}{6} (k_B T)^2 D'(\mu) + \dots$$

since we expect $\mu(T) \approx \varepsilon_F$, the second term is approximately equal to the integrand \times the range of integration, and the last term can be evaluated at ε_F

$$0 \approx D(\varepsilon_F)(\mu - \varepsilon_F) + \frac{\pi^2}{6} (k_B T)^2 D'(\varepsilon_F) + \dots$$

Question 2: Solve for $\mu(T)$ to leading order in T , expressing your answer in terms of ε_F , T , and constants only.

Solving the previous expression: $\mu(T) \approx \varepsilon_F - \frac{\pi^2}{6} (k_B T)^2 \frac{D'(\varepsilon_F)}{D(\varepsilon_F)}$

$$D(\varepsilon_F) = \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \varepsilon_F^{1/2} \quad D'(\varepsilon_F) = \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \frac{1}{2\varepsilon_F^{1/2}} = \frac{D(\varepsilon_F)}{2\varepsilon_F}$$

Therefore,

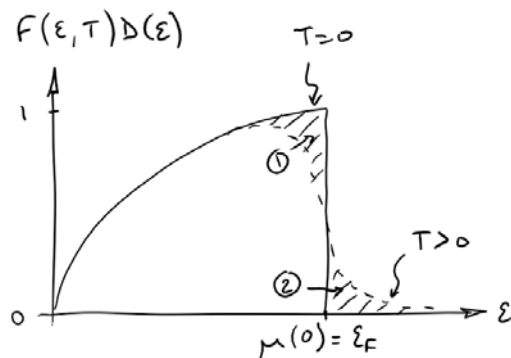
$$\mu(T) = \varepsilon_F - \frac{\pi^2}{12} \left(\frac{k_B T}{\varepsilon_F} \right) k_B T + \dots$$

So $\mu(T)$ decreases from $\mu(0) = \varepsilon_F$ quadratically with temperature T . Since $k_B T \ll \varepsilon_F$, this is a very small correction.

Why does the chemical potential decrease with T ? Here's a way to visualize it graphically

$$N = \int_0^\infty d\varepsilon D(\varepsilon) f(\varepsilon, T) \text{ must be true for all } T$$

i.e. the area under the curve $D(\varepsilon)f(\varepsilon, T)$ must always be equal to N , for all T



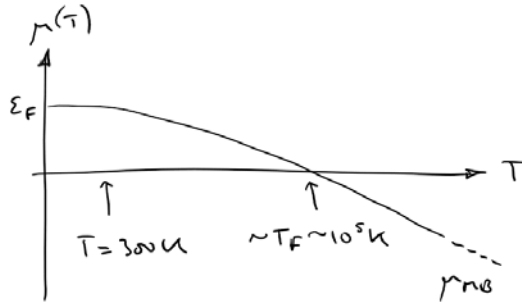
Suppose $\mu(T > 0) = \mu(0)$ as shown to the left. Since the areas under the curve for $T > 0$ and $T = 0$ must be equal, the shaded areas ① and ② must be equal.

However, clearly area ① < area ② in the plot, so the area under the putative $D(\varepsilon)f(\varepsilon, T > 0) > D(\varepsilon)f(\varepsilon, 0)$ which cannot be the case.

The only way the areas can be the same is if the midpoint of the curve for $T > 0$ is shifted to the left, i.e. $\mu(T > 0) < \mu(0)$

Here's a more physical way to look at it: $\mu(T) = \left(\frac{\partial F}{\partial N} \right)_{T,V}$ and $F = U - TS$

When T increases from 0, we expect U to increase due to additional thermal energy. However, S also increases, because energy levels above ε_F are now accessible and there are many ways to fill them. The increase in S exceeds that of U , so F and μ decrease.



$\mu(T)$ decreases from quadratically with temperature T .

At very high temperatures $T \gg T_F$, we must get back classical $\mu(T) = \mu_{MB}$

Now calculate energy U

$$\begin{aligned}
 U(T) &= \int_0^\infty d\varepsilon \varepsilon D(\varepsilon) f(\varepsilon, T) = \int_0^\mu d\varepsilon \varepsilon D(\varepsilon) + \frac{\pi^2}{6} (k_B T)^2 \frac{d}{d\varepsilon} (\varepsilon D(\varepsilon)) \Big|_\mu + \dots \\
 &= \underbrace{\int_0^{\varepsilon_F} d\varepsilon \varepsilon D(\varepsilon)}_{\frac{3}{5} N \varepsilon_F} + \underbrace{\int_{\varepsilon_F}^\mu d\varepsilon \varepsilon D(\varepsilon)}_{\approx \varepsilon_F D(\varepsilon_F) (\mu - \varepsilon_F)} + \frac{\pi^2}{6} (k_B T)^2 \underbrace{(D(\mu) + \mu D'(\mu))}_{\approx D(\varepsilon_F) + \varepsilon_F D'(\varepsilon_F)} + \dots
 \end{aligned}$$

In the last term we substituted $\mu(T) \approx \varepsilon_F$, which is correct to lowest order.

Question 3: Solve for $U(T)$ using $\mu(T)$ from the previous section to leading order in T , expressing your answer in terms of ε_F , T , and constants only.

Plugging in for μ in the second term and using the fact that $D'(\varepsilon_F) = D(\varepsilon_F)/2\varepsilon_F$:

$$\begin{aligned}
 U(T) &= U(0) - \frac{\pi^2}{12} \frac{(k_B T)^2}{\cancel{\varepsilon_F}} \cancel{D(\varepsilon_F)} + \frac{\pi^2}{6} (k_B T)^2 D(\varepsilon_F) + \frac{\pi^2}{6} (k_B T)^2 \cancel{\frac{D(\varepsilon_F)}{2\varepsilon_F}} + \dots \\
 &= U(0) + \frac{\pi^2}{6} (k_B T)^2 D(\varepsilon_F) + \dots
 \end{aligned}$$

It's convenient to write this expression in terms of N

$$\varepsilon_F = \frac{\hbar^2}{2m} \left(3\pi^2 \frac{N}{V} \right)^{2/3} \quad D(\varepsilon_F) = \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \varepsilon_F^{1/2} = \frac{3}{2} \frac{N}{\varepsilon_F}$$

$$\text{So, } U(T) = U(0) + \frac{\pi^2}{4} N k_B T \left(\frac{k_B T}{\varepsilon_F} \right) + \dots$$

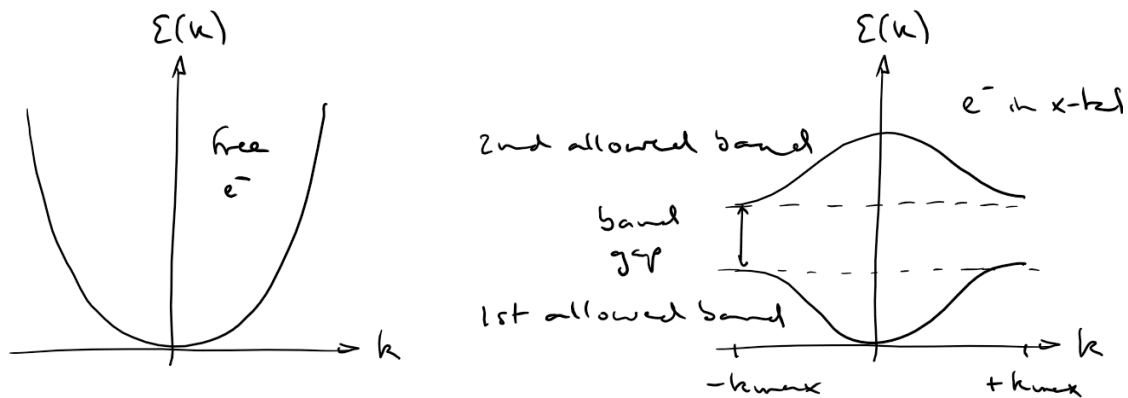
Now we can solve for the heat capacity: $C_V = \frac{\pi^2}{2} N k_B \frac{k_B T}{\varepsilon_F} = \gamma T$ which gives the linear T dependence seen experimentally.

For many metals (e.g. alkali metals), $\gamma = \frac{\pi^2}{2} \frac{Nk_B^2}{\varepsilon_F}$ is accurate to ~20-30%

Realistic materials

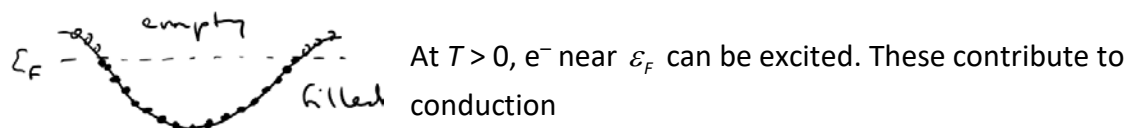
We assumed e^- in metal are “free” with energy $\varepsilon(k) = \frac{\hbar^2 k^2}{2m}$

When accounting for electrostatic potential from ions in crystal lattice, e^- energy is more complicated:

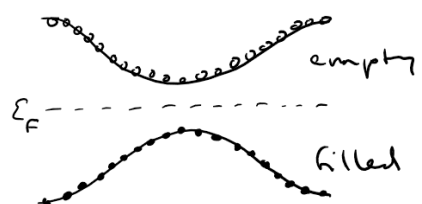


In real crystals, there are allowed and forbidden energy “bands” that create energy gaps

For a metal – ε_F is within one band



For an insulator – ε_F is in energy gap between two bands



Here, there are no empty states close to occupied states, so e^- are “stuck” in place and cannot conduct electricity.

In semiconductors, the gap is $\sim k_B T$ so a few e^- can jump across the gap thermally