Non-interacting fermions

Two class of experimental systems

- Electrons are Fermions
- He3 are Fermions

Bosons and Fermions

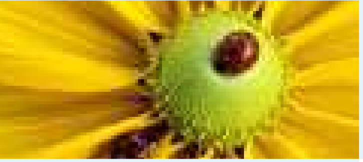
- There are two types of particles in nature.
- In quantum mechanics, energies are discrete variables. We can label them by a subscript.
- For Fermions (Bosons), for any energy e_i, at most one (no limit) particles can have that energy.

Non-interacting Fermions

- For g the grand canonical potential,
- $e^{-g\beta} = \sum_{[n]} \exp\text{-}\{\beta[n_1(e_1-\mu)+n_2(e_2-\mu)+\ldots]\} = \sum_{n_1} \exp\text{-}[\beta\, n_1(e_1-\mu)] \sum_{n_2} \exp\text{-}[\beta\, n_2(e_2-\mu)] \ldots$
- $\sum_n e^{-\beta(e-\mu)} = 1+e^{-\beta(e-\mu)}$.
- Hence $e^{-g\beta}=\prod_i [1+e^{-\beta(e_i-\mu)}]$.
- $g= -\sum_i \ln [1+e^{-\beta(e_i-\mu)}]/ \beta$.

- e=$\frac{p^2}{2m}$, Define $\alpha = e^{\beta\mu}$
- $g = -kTV \int d^3p \ \ln\left[1 + \alpha e^{-\beta p^2/2m}\right]/h^3$
- h^3 is from quantum mechanics.
- The density $\rho = \dfrac{<N>}{V} = -\partial\, \beta\, g/\partial(\beta\mu)/V$
- $\rho = \int d^3p\alpha e^{-\beta p^2/2m} / \left[1 + \alpha e^{-\beta p^2/2m}\right]/h^3$
- $= \int d^3p \,/ \left[1 + e^{(\frac{\beta p^2}{2m} - \mu)}\right]$

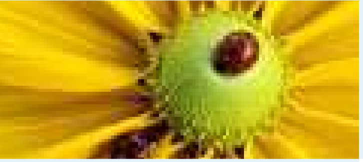
- e=$\frac{p^2}{2m}$,
- $\rho = \int d^3p \,/h^3/\left[1 + e^{(e-\mu)}\right]$
- $f(e) = 1/\left[1 + e^{(e-\mu)}\right]$ is called the Fermi distribution function.
- $d^3p/h^3 = \frac{4\pi p^2 dp}{h^3} = g(e)de$, g(e) is called the density of states
- $g(e) = \frac{2\pi(2m)^{3/2}e^{1/2}}{h^3}$
- $\rho = \int de \; g(e)f(e)$



Thermodynamics

- We found that the thermodynamic properties of a system of non-interacting fermions can be obtained from the Landau potential

$$\begin{aligned}\Phi &= -k_{\mathrm{B}}T\log Z_G \\ &= -k_{\mathrm{B}}T\sum_\alpha \log\{1+\exp[\beta(\mu-\varepsilon_\alpha)]\}.\end{aligned}$$



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- For example, the mean number of particles and the mean energy are

$$\langle N\rangle = \sum_\alpha \langle n_\alpha\rangle, \qquad \langle E\rangle = \sum_\alpha \langle n_\alpha\rangle \varepsilon_\alpha,$$

in which the mean number of particles occupying the single-particle state α is

$$\langle n_\alpha\rangle = \frac{1}{\exp[\beta(\varepsilon_\alpha-\mu)]+1}.$$

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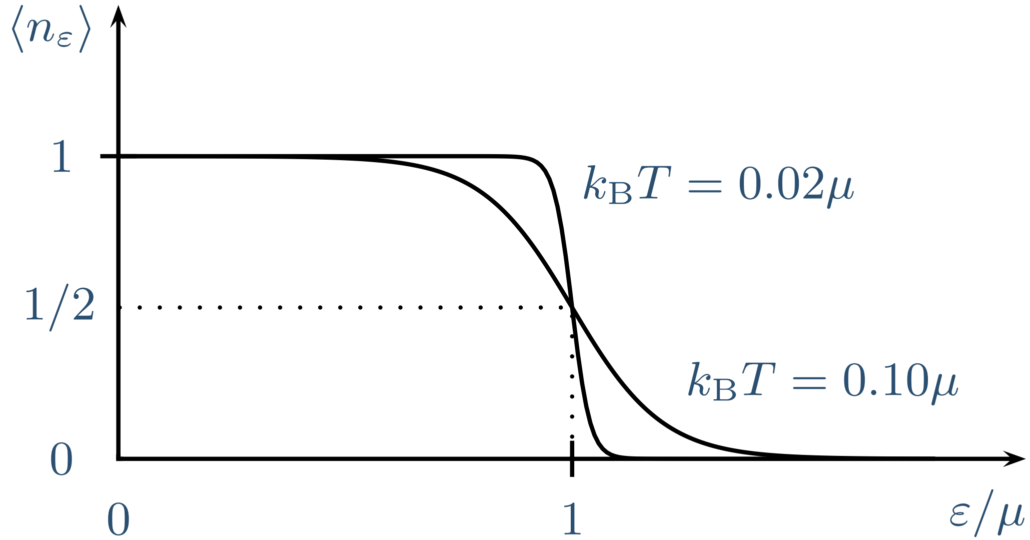
- Since the exponential function is never negative, we have

$$\langle n_\alpha\rangle \le 1,$$

which is crucially different from the boson case.

- The Fermi–Dirac occupancy function $\langle n_\varepsilon \rangle$ is plotted below for two different temperatures:



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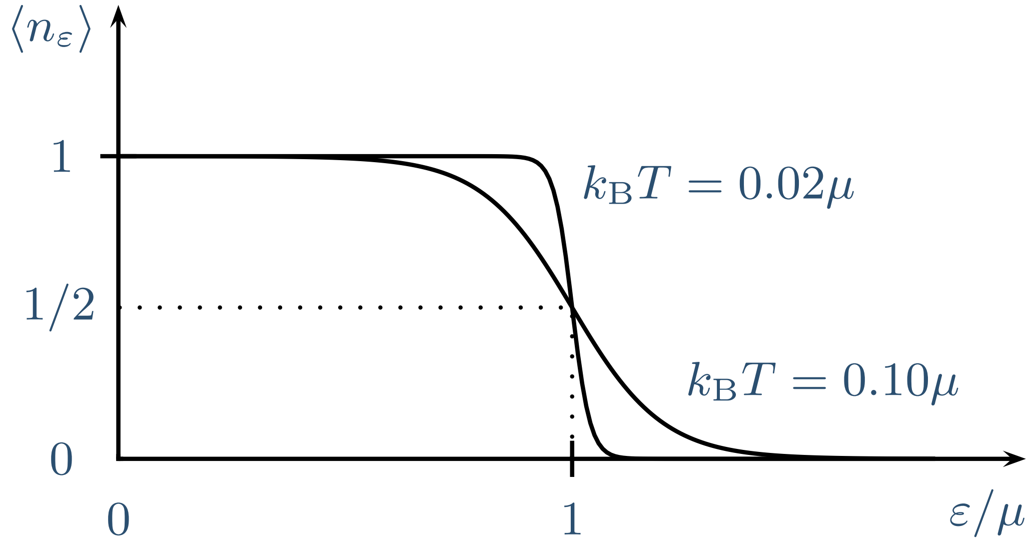

- Note that the chemical potential μ depends on T.
- The value of μ is usually fixed by the particle-number condition

$$\langle N \rangle = \int_0^\infty \langle n_\varepsilon \rangle g(\varepsilon)\, \mathrm{d}\varepsilon, \qquad \langle n_\varepsilon \rangle = \frac{1}{\exp[\beta(\varepsilon - \mu)] + 1}.$$

Free electrons

- For free fermions of spin s, the density of states is

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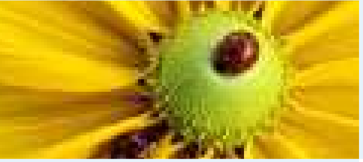
- The case of free electrons ($s = 1/2$) is particularly relevant for the study of metals.
- The particle-number condition is then

$$\langle N\rangle = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\int_0^\infty \frac{\varepsilon^{1/2}\,\mathrm{d}\varepsilon}{\exp[\beta(\varepsilon-\mu)]+1}.$$



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- As an exercise, you will show that the density $n = \langle N\rangle/V$ satisfies

$$n\Lambda^3 = (2s+1)f_{3/2}(z), \qquad z \equiv \exp\beta\mu,$$

where $f_\nu(z)$ is the Fermi–Dirac integral

$$f_\nu(z) = \frac{1}{\Gamma(\nu)}\int_0^\infty \frac{x^{\nu-1}\,\mathrm{d}x}{z^{-1}\exp x + 1} = \sum_{k=1}^{\infty}(-1)^{k-1}\frac{z^k}{k^\nu}.$$

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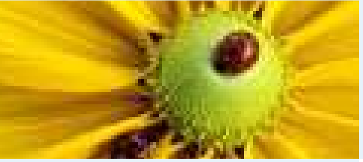
- Let us suppose that when $T \to 0$, the chemical potential has a well defined limit:

$$\lim_{T \to 0} \mu(T) = \mu_0.$$



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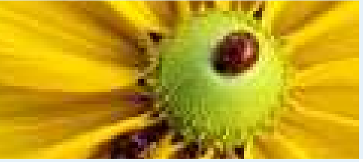

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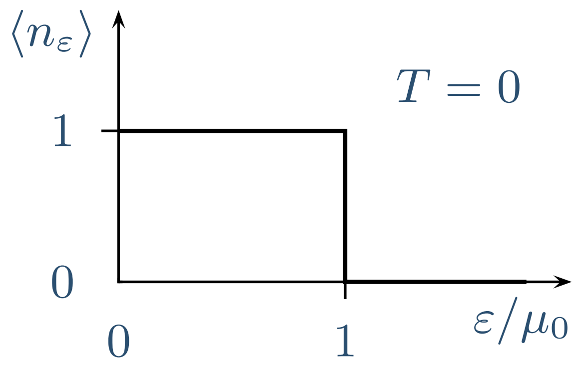
- From this, we see that the occupancy function $\langle n_\varepsilon \rangle$ is a step function with a discontinuity at $\varepsilon = \mu_0$:



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- To estimate the magnitude of μ_0, we can use atomic units:

$$\mu_0 = \frac{\hbar^2}{me^2}\frac{e^2}{2}(3\pi^2 n)^{2/3}$$
$$= a_0 \frac{e^2}{2}(3\pi^2 n)^{2/3}$$
$$= \frac{e^2}{2a_0}(3\pi^2 n a_0^3)^{2/3}.$$

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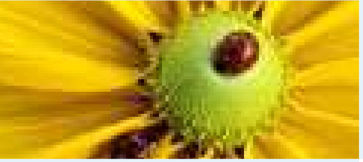
$$3\pi^2 n a_0^3 \lesssim O(1).$$



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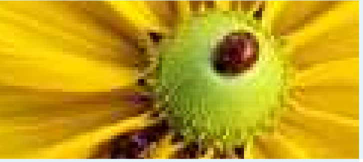
- The low-temperature chemical potential is therefore

$$\begin{aligned}\mu_0 &= \frac{e^2}{2a_0} \times O(1)\\ &\sim 13.6\ \mathrm{eV}\\ &= 1.58 \times 10^5\ \mathrm{K}\,.\end{aligned}$$

- This number is huge on the scale of $T \approx 300$ K or $k_\mathrm{B}T \approx 0.0259$ eV.



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- As T increases, $\mu(T)$ decreases, eventually reaching the classical limit when $k_\mathrm{B}T \gg \mu_0$.
- Unlike the boson case, nothing interesting happens when $\mu(T) \approx 0$.

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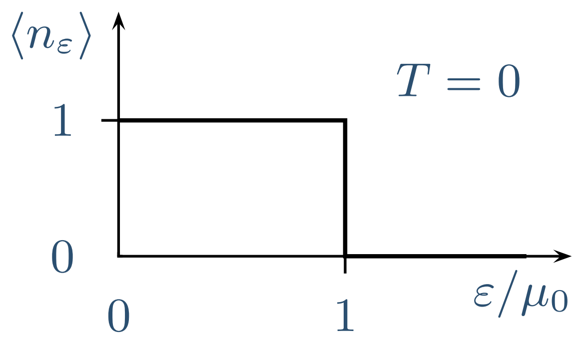

- The derivative of $\langle n_\varepsilon \rangle$ is therefore a Dirac delta function:

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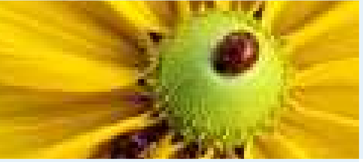

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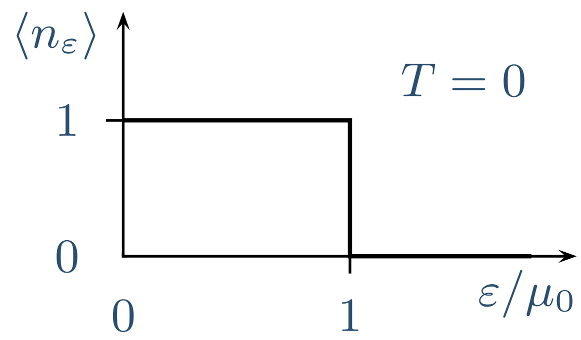

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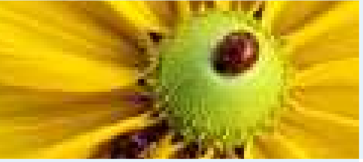
- For $T > 0$, we can also define a "Fermi delta function"

$$\Delta(\varepsilon) \equiv -\frac{\partial}{\partial \varepsilon}\langle n_\varepsilon \rangle.$$

Fermi delta function

- The Fermi delta function is given explicitly by

$$\begin{aligned}\Delta(\varepsilon) &= -\frac{\partial}{\partial\varepsilon}\left(\frac{1}{\exp[\beta(\varepsilon-\mu)]+1}\right)\\ &= \left(\frac{1}{\exp[\beta(\varepsilon-\mu)]+1}\right)^2 \beta\exp[\beta(\varepsilon-\mu)]\\ &= \frac{1}{4k_{\mathrm{B}}T}\,\frac{1}{\cosh^2[\beta(\varepsilon-\mu)/2]}.\end{aligned}$$



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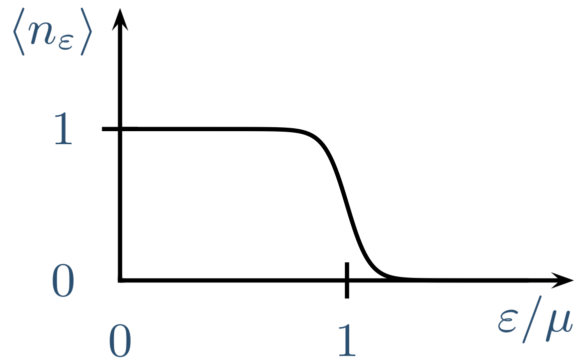

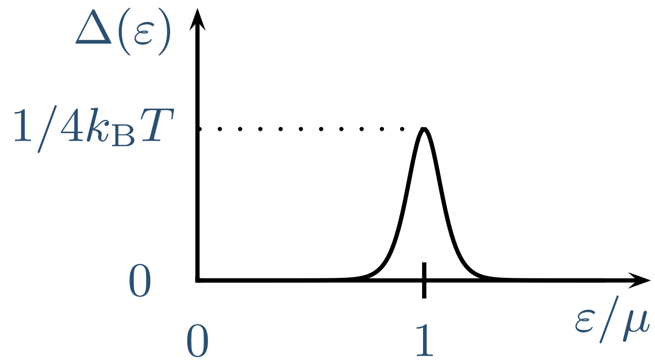

- This is an exponentially localized function with unit area, height $1/4k_{\mathrm{B}}T$, and width $\sim 4k_{\mathrm{B}}T$.

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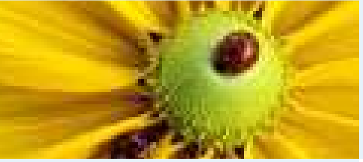
$$\int_0^\infty y(\varepsilon)\Delta(\varepsilon)\,\mathrm{d}\varepsilon,$$

where $y(\varepsilon)$ is a smooth function of ε.



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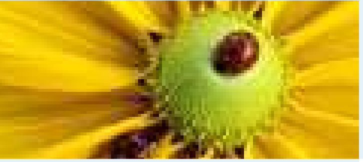
- If $k_{\mathrm{B}}T \ll \mu_0$, $\Delta(\varepsilon)$ has a sharp peak at $\varepsilon = \mu$, so we can extend the lower limit of integration to $-\infty$ with negligible error.
- All odd powers of $(\varepsilon - \mu)$ then integrate to zero, because $\Delta(\varepsilon)$ is an even function of $(\varepsilon - \mu)$.

- For the even powers of $(\varepsilon - \mu)$, we get[1]

$$\int_{-\infty}^{\infty} (\varepsilon - \mu)^n \Delta(\varepsilon)\, d\varepsilon = 2(k_B T)^n n!(1 - 2^{-n+1})\zeta(n) \qquad (n \text{ even}).$$



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$$\int_0^{\infty} y(\varepsilon)\Delta(\varepsilon)\,\mathrm{d}\varepsilon = y(\mu) + \frac{\pi^2}{6}(k_\mathrm{B}T)^2 y''(\mu) + \frac{7\pi^4}{360}(k_\mathrm{B}T)^4 y^{(4)}(\mu) + \cdots .$$

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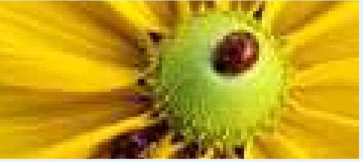
- We can also write this as

$$\Delta(\varepsilon) = \delta(\varepsilon - \mu) + \frac{\pi^2}{6}(k_\mathrm{B}T)^2 \delta''(\varepsilon - \mu) + \frac{7\pi^4}{360}(k_\mathrm{B}T)^4 \delta^{(4)}(\varepsilon - \mu) + \cdots ,$$

with the understanding that this expression is to be used only inside an integral.

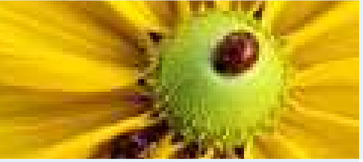
[1] R. Kubo, *Statistical Mechanics* (North–Holland, 1967), pp. 231–233.



Chemical potential

- We can now use this approach to find the chemical potential $\mu(T)$ for $k_{\mathrm{B}}T \ll \mu_0$.
- As we found above, the condition that determines $\mu(T)$ is

$$\langle N \rangle = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \int_0^\infty \varepsilon^{1/2} \langle n_\varepsilon \rangle \, \mathrm{d}\varepsilon.$$



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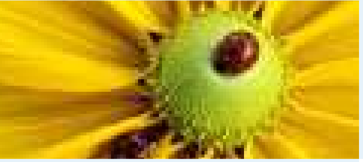
- But we also know that

$$\langle N\rangle = \frac{V}{3\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\mu_0^{3/2}.$$

- Hence, the first integral can be written as

$$\mu_0^{3/2} = \frac{3}{2}\int_0^\infty \varepsilon^{1/2}\langle n_\varepsilon\rangle\,\mathrm{d}\varepsilon.$$



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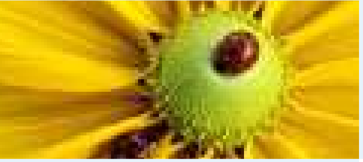
- Hence, the first integral can be written as

$$\mu_0^{3/2} = \frac{3}{2} \int_0^\infty \varepsilon^{1/2} \langle n_\varepsilon \rangle \, \mathrm{d}\varepsilon.$$

- Upon integrating by parts, we find

$$\mu_0^{3/2} = -\frac{3}{2} \int_0^\infty \left(\frac{2}{3}\varepsilon^{3/2}\right) \frac{\partial \langle n_\varepsilon \rangle}{\partial \varepsilon} \, \mathrm{d}\varepsilon = \int_0^\infty \varepsilon^{3/2} \Delta(\varepsilon) \, \mathrm{d}\varepsilon.$$



Expansions

- We can now use the Sommerfeld expansion with $y(\varepsilon) = \varepsilon^{3/2}$, obtaining

$$\begin{aligned}
\mu_0^{3/2} &= \int_0^\infty \varepsilon^{3/2} \Delta(\varepsilon)\, \mathrm{d}\varepsilon \\
&= \mu^{3/2} + \frac{\pi^2}{6}(k_\mathrm{B}T)^2 \left(\frac{3}{4}\mu^{-1/2}\right) + \frac{7\pi^4}{360}(k_\mathrm{B}T)^4 \left(\frac{9}{16}\mu^{-5/2}\right) + \cdots \\
&= \mu^{3/2}\left[1 + \frac{\pi^2}{8}\left(\frac{k_\mathrm{B}T}{\mu}\right)^2 + \frac{7\pi^4}{640}\left(\frac{k_\mathrm{B}T}{\mu}\right)^4 + \cdots\right].
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- Upon bringing $\mu^{3/2}$ over to the left side, we find

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\mu = \mu_0\left[1 + \frac{\pi^2}{8}\left(\frac{k_\mathrm{B}T}{\mu}\right)^2 + \frac{7\pi^4}{640}\left(\frac{k_\mathrm{B}T}{\mu}\right)^4 + \cdots\right]^{-2/3}.
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- A power series expansion then gives

$$\mu = \mu_0 \left[1 - \frac{\pi^2}{12}\left(\frac{k_\mathrm{B}T}{\mu}\right)^2 + \frac{\pi^4}{720}\left(\frac{k_\mathrm{B}T}{\mu}\right)^4 + \cdots\right].$$

Final chemical potential

- Finally, we can iterate this expression to obtain

$$\mu = \mu_0 \left[1 - \frac{\pi^2}{12} \left(\frac{k_{\rm B} T}{\mu_0} \right)^2 - \frac{\pi^4}{80} \left(\frac{k_{\rm B} T}{\mu_0} \right)^4 - \cdots \right],$$

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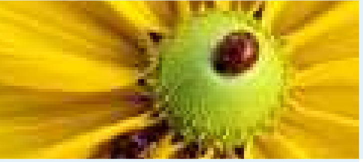
- For typical metals, we have

$$\mu_0 \sim 10^4\text{–}10^5 \ \mathrm{K}.$$



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- Hence, at room temperature ($T \sim 300\ \mathrm{K}$), the fractional change is

$$\frac{\Delta\mu}{\mu_0} \sim \left(\frac{300}{10^4\text{–}10^5} \right)^2 \sim \frac{10^5}{10^8\text{–}10^{10}} \sim 10^{-3}\text{–}10^{-5},$$

which is very small.

Heat capacity

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$$C_V = \left(\frac{\partial U}{\partial T}\right)_{V,N},$$

where the internal energy is

$$\begin{aligned} U = \langle E \rangle &= \int_0^\infty \varepsilon g(\varepsilon) \langle n_\varepsilon \rangle \, \mathrm{d}\varepsilon \\ &= \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \int_0^\infty \varepsilon^{3/2} \langle n_\varepsilon \rangle \, \mathrm{d}\varepsilon. \end{aligned}$$

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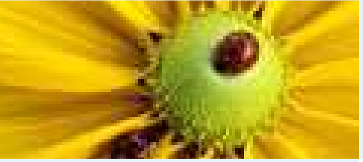
- Here we can divide by $\langle N \rangle$ (i.e., N in thermodynamic notation) to get rid of some constants:

$$\frac{U}{N} = \frac{3}{2}\mu_0^{-3/2} \int_0^\infty \varepsilon^{3/2} \langle n_\varepsilon \rangle \, \mathrm{d}\varepsilon.$$



Internal energy

- We can now integrate by parts as before to obtain

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\begin{aligned}
\frac{U}{N} &= \frac{3}{2}\mu_0^{-3/2}\int_0^\infty \left(\frac{2}{5}\varepsilon^{5/2}\right)\left(-\frac{\partial\langle n_\varepsilon\rangle}{\partial\varepsilon}\right)\mathrm{d}\varepsilon \\
&= \frac{3}{5}\mu_0^{-3/2}\int_0^\infty \varepsilon^{5/2}\Delta(\varepsilon)\,\mathrm{d}\varepsilon.
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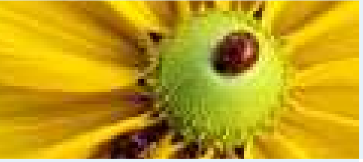
- The Sommerfeld expansion then gives

$$\begin{aligned}\frac{U}{N} &= \frac{3}{5}\mu_0^{-3/2}\int_0^\infty \varepsilon^{5/2}\left[\delta(\varepsilon-\mu)+\frac{\pi^2}{6}(k_\mathrm{B}T)^2\delta''(\varepsilon-\mu)+\cdots\right]\mathrm{d}\varepsilon \\ &= \frac{3}{5}\mu_0^{-3/2}\left[\mu^{5/2}+\frac{\pi^2}{6}(k_\mathrm{B}T)^2\left(\frac{5}{2}\right)\left(\frac{3}{2}\right)\mu^{1/2}+O(k_\mathrm{B}T)^4\right].\end{aligned}$$



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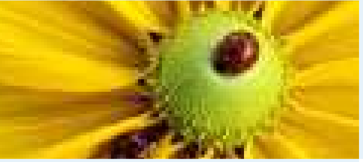
- At $T=0$, the energy per particle is simply

$$\frac{U}{N}=\frac{3}{5}\mu_0.$$

- The ground-state energies of electron systems are therefore enormous ($\mu_0 \sim 10^5$ K), which is important in the stability of matter.



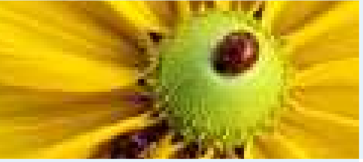
Final internal energy

- For the case $T > 0$, our previous result for the chemical potential

$$\frac{\mu}{\mu_0} \approx 1 - \frac{\pi^2}{12}\left(\frac{k_{\mathrm{B}}T}{\mu_0}\right)^2$$

gives

$$\left(\frac{\mu}{\mu_0}\right)^{5/2} \approx 1 - \frac{5}{2}\left(\frac{\pi^2}{12}\right)\left(\frac{k_{\mathrm{B}}T}{\mu_0}\right)^2.$$



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- The internal energy then becomes

$$\begin{aligned}\frac{U}{N} &\approx \frac{3}{5}\mu_0\left[1 - \frac{5\pi^2}{24}\left(\frac{k_\mathrm{B}T}{\mu_0}\right)^2 + \frac{5\pi^2}{8}\left(\frac{k_\mathrm{B}T}{\mu_0}\right)^2\right] \\ &\approx \frac{3}{5}\mu_0\left[1 + \frac{5\pi^2}{12}\left(\frac{k_\mathrm{B}T}{\mu_0}\right)^2\right].\end{aligned}$$

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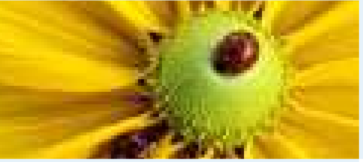
- Continuing the expansion one term further, we get

$$\frac{U}{N} = \frac{3}{5}\mu_0\left[1 + \frac{5\pi^2}{12}\left(\frac{k_{\rm B}T}{\mu_0}\right)^2 - \frac{\pi^4}{16}\left(\frac{k_{\rm B}T}{\mu_0}\right)^4 + \cdots\right].$$

Heat capacity

- To connect with experiment, we can now calculate the heat capacity

$$
\begin{aligned}
C_V &= \left(\frac{\partial U}{\partial T}\right)_{V,N} = \frac{k_\mathrm{B}}{\mu_0}\left(\frac{\partial U}{\partial (k_\mathrm{B}T/\mu_0)}\right)_{V,N} \\
&= \frac{3}{5}Nk_\mathrm{B}\frac{\partial}{\partial(k_\mathrm{B}T/\mu_0)}\left[1+\frac{5\pi^2}{12}\left(\frac{k_\mathrm{B}T}{\mu_0}\right)^2-\frac{\pi^4}{16}\left(\frac{k_\mathrm{B}T}{\mu_0}\right)^4+\cdots\right] \\
&= \frac{3}{5}Nk_\mathrm{B}\left[\frac{5\pi^2}{12}(2)\left(\frac{k_\mathrm{B}T}{\mu_0}\right)-\frac{\pi^4}{16}(4)\left(\frac{k_\mathrm{B}T}{\mu_0}\right)^3+\cdots\right].
\end{aligned}
$$



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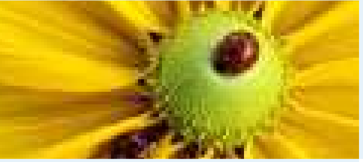
\end{aligned}
$$

- We can write this as

$$
C_V = \frac{3}{2}Nk_\mathrm{B}\left[\frac{\pi^2}{3}\left(\frac{k_\mathrm{B}T}{\mu_0}\right) - \frac{\pi^4}{10}\left(\frac{k_\mathrm{B}T}{\mu_0}\right)^3 + \cdots\right],
$$

  where $(3/2)Nk_\mathrm{B}$ is the classical result.
- Hence, at small T, the classical heat capacity is reduced by a factor of

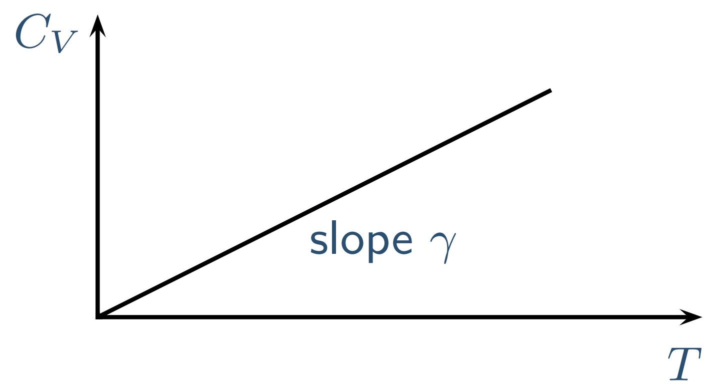
$$
\frac{\pi^2}{3}\left(\frac{k_\mathrm{B}T}{\mu_0}\right) \ll 1.
$$



Predicted behavior

- Thus, we now have a prediction for the low-temperature ($k_\mathrm{B}T \ll \mu_0$) heat capacity of free and independent electrons:

$$C_V = \gamma T + O(T^3), \qquad \gamma = \frac{3}{2} N k_\mathrm{B} \left(\frac{\pi^2}{3} \frac{k_\mathrm{B}}{\mu_0} \right).$$



- How does this compare with experiment?