CHM 421/621 Statistical Mechanics

Lecture 30 Perfect Fermi Gas

Applications of Statistical Mechanics

Lecture Plan

Perfect Fermi Gas (Electrons in a metal)

Rotational partition function for homonuclear diatomic

Application to Chemical Equilibrium

Applications

Summary of Quantum Statistics

$$Z_g = \prod_{i=0}^{\infty} \left(1 \pm e^{\beta(\mu - \epsilon_i)}\right)^{\pm 1}$$

$$\overline{n}_i = \frac{1}{e^{-\beta(\mu-\epsilon_i)} \pm 1}$$

+ Fermi-Dirac

- Bose-Einstein

Classical limit: High temperature or low density $\lambda \to 0$

$$\overline{n}_i \approx \lambda e^{-\beta \epsilon_i} \quad \Rightarrow \quad \frac{\overline{n}_i}{N} = \frac{e^{-\beta\epsilon_i}}{z}$$

Applications

Perfect Fermi gas

Consider a gas of *N* electrons in a cubic box of side *L* at a temperature *T*

Treating this system like the ideal gas we have

$$\epsilon(\vec{k}) = \frac{\hbar^2 k^2}{2m} \qquad k_\alpha = \frac{n_\alpha \pi}{L} \quad (\alpha = x, y, z)$$

$$n_\alpha = 1, 2, 3, \ldots$$

Further each electron can be in one of two spin states $\sigma = +1/2, -1/2$

$$\sum_i \to \sum_\sigma \left(\frac{L}{\pi}\right)^3 \int d^3k$$

Therefore, the average number of electrons in the system is

$$\overline{N} = \sum_\sigma \left(\frac{L}{\pi}\right)^3 \int d^3k \left(1 + e^{-\beta(\mu - \epsilon(\vec{k}))}\right)^{-1}$$

$$= 2\left(\frac{L}{\pi}\right)^3 \int d^3k \left(1 + e^{-\beta(\mu - \epsilon(\vec{k}))}\right)^{-1}$$

Applications

Perfect Fermi gas

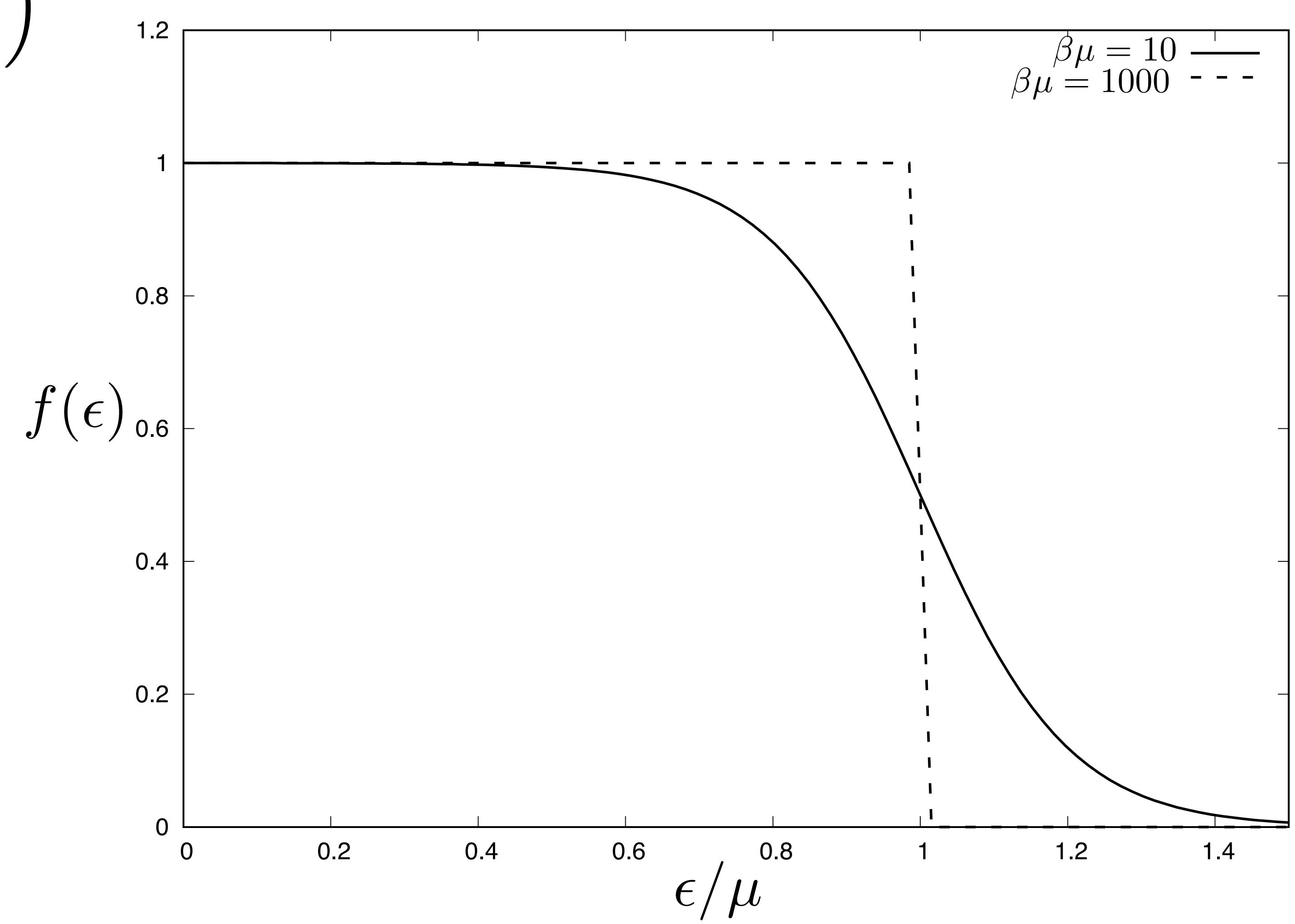
Transforming the integral to energy as a continuous variable and using the density of states

$$\overline{N} = \int_0^\infty d\epsilon \; g(\epsilon) \left(1 + e^{-\beta(\mu-\epsilon)}\right)^{-1}$$

$$g(\epsilon) = 4\pi \left(\frac{2m}{h^2}\right)^{\frac{3}{2}} V \epsilon^{\frac{1}{2}}$$

$$f(\epsilon) = \frac{1}{1 + e^{-\beta(\mu-\epsilon)}}$$

Fermi-Dirac distribution function



Applications

Perfect Fermi gas

For T -> 0 all states below a certain energy μ_0 are occupied while others are vacant

$$\overline{N} = \int_0^{\mu_0} d\epsilon \; g(\epsilon)$$

$$= \pi \left(\frac{2m}{h^2}\right)^{\frac{3}{2}} V \int_0^{\mu_0} d\epsilon \; \epsilon^{\frac{1}{2}}$$

$$= \frac{8\pi}{3} \left(\frac{2m}{h^2}\right)^{\frac{3}{2}} V \mu_0^{\frac{3}{2}}$$

$$\mu_0 = \frac{h^2}{2m} \left(\frac{3}{8\pi}\right)^{\frac{2}{3}} \left(\frac{N}{V}\right)^{\frac{2}{3}}$$ Fermi energy

Applications

Perfect Fermi gas

Table 9.5.1: Conduction Electron Densities and Fermi Energies for Some Metals

Element	Conduction Band Electron Density $(10^{28}\, m^{-3})$	Free-Electron Model Fermi Energy (eV)
Al	18.1	11.7
Ba	3.15	3.64
Cu	8.47	7.00
Au	5.90	5.53
Fe	17.0	11.1
Ag	5.86	5.49

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Applications

Perfect Fermi gas

Average energy of system

$$\overline{E} \approx \int_0^{\mu_0} d\epsilon \; g(\epsilon)\epsilon$$

$$= 4\pi \left(\frac{2m}{h^2}\right)^{\frac{3}{2}} V \int_0^{\mu_0} \epsilon^{\frac{3}{2}}$$

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

Clearly, there is no equipartition of energy here

Pressure in system

$$P = \frac{k_B T}{V} \sum_i \ln(1 + \lambda e^{-\beta\epsilon_i})$$

$$\longrightarrow 2k_B T \frac{1}{\pi^3} \int d^3k \;\; \ln(1 + \lambda e^{-\beta\epsilon(\vec{k})})$$

$$P = 4\pi k_B T \left(\frac{2m}{h^2}\right)^{\frac{3}{2}} \int_0^{\mu_0} d\epsilon \; \epsilon^{\frac{1}{2}} \ln(1 + e^{\beta(\mu - \epsilon)})$$

$$\approx 4\pi \left(\frac{2m}{h^2}\right)^{\frac{3}{2}} \int_0^{\mu_0} d\epsilon \; \epsilon^{\frac{1}{2}} \, (\mu_0 - \epsilon) = \frac{2}{5} N\mu_0 / V \qquad (\beta \to \infty)$$

Zero-point pressure is $O(10^6)$ atm. This is completely quantum effect.

Applications

Perfect Fermi Gas

All average properties on the Fermi gas can be expressed as

$$I = \int_0^\infty f(\epsilon)h(\epsilon)$$

$$= -\int_0^\infty f'(\epsilon)H(\epsilon)$$

Integration by parts where $H(\epsilon) = \int_0^\epsilon d\epsilon\ h(\epsilon)$

↓

Sharply peaked around μ. So we can Taylor expand *H* around it.

$$H(\epsilon) = H(\mu) + (\epsilon - \mu)\left(\frac{\partial H}{\partial \epsilon}\right)_{\epsilon=\mu} + \frac{1}{2}(\epsilon - \mu)^2\left(\frac{\partial^2 H}{\partial \epsilon^2}\right)_{\epsilon=\mu} + \cdots$$

Applications

Perfect Fermi Gas

Substitution gives

$$I = H(\mu)L_0 + \left(\frac{\partial H}{\partial \epsilon}\right)_{\epsilon=\mu} L_1 + \frac{1}{2}\left(\frac{\partial^2 H}{\partial \epsilon^2}\right)_{\epsilon=\mu} L_2 + \cdots \quad \text{where} \quad L_j = \frac{1}{\beta^j}\int_{-\infty}^{\infty} \frac{x^j e^x}{(1+e^x)^2} dx$$

Integrand in L_j is an even function of *j*. => $L_1=L_3=L_5=\ldots=0$

$$L_0 = 1$$

$$L_2 = \frac{\pi^2}{3\beta^2}$$

Applications

Perfect Fermi Gas

Average number of particles

$$h(\epsilon) = 4\pi(2m/h^2)^{\frac{3}{2}} V \epsilon^{\frac{1}{2}}$$

$$\overline{N} = \frac{8\pi}{3}\left(\frac{2m}{h^2}\right)^{\frac{3}{2}} V\mu^{\frac{3}{2}}\left[1 + \frac{\pi^2}{8}(\beta\mu)^{-2} + \cdots\right]$$

$$\implies \mu_0 = \mu\left[1 + \frac{\pi^2}{8}(\beta\mu)^{-2} + \cdots\right]^{\frac{2}{3}}$$

Using $\mu_0 = \frac{h^2}{2m}\left(\frac{3}{8\pi}\right)^{\frac{2}{3}}\left(\frac{N}{V}\right)^{\frac{2}{3}}$

Let $\eta = (\beta\mu_0)^{-1}$

$$\implies \mu = \mu_0\left[1 - \frac{\pi^2}{12}\eta^2 + \cdots\right]$$

Applications

Perfect Fermi Gas

Average energy of particles

$$E = E_0 \left(\frac{\mu}{\mu_0}\right)^{\frac{5}{2}} \left[1 + \frac{5}{8}\pi^2(\beta\mu)^{-2} + \cdots\right]$$

$$= E_0 \left[1 + \frac{5\pi^2}{12}\eta^2 + \cdots\right]$$

Specific heat

$$C_V = \frac{\pi^2 N k_B T}{2(\mu_0/k)} = \frac{\pi^2}{2} N k_B \left(\frac{T}{T_F}\right)$$

~ 10^{-4} *T* cal/deg-mole for many metals

$T_F = \mu_0/k_b$ Fermi temperature

$$\boxed{C_V \sim T}$$

For electrons in a metal