

1) First quantum correction to pressure

$$a) f(\epsilon) = \frac{1}{e^{(\epsilon-\mu)/T} \pm 1} = \frac{1}{e^{(\epsilon-\mu)/T} (1 \pm e^{-(\epsilon-\mu)/T})}$$

$$\approx e^{-(\epsilon-\mu)/T} (1 \mp e^{-(\epsilon-\mu)/T}) = e^{-(\epsilon-\mu)/T} \mp e^{-2(\epsilon-\mu)/T} \quad \begin{array}{l} \text{- Fermi} \\ \text{+ Bose} \end{array}$$

$$b) N = \int_0^\infty d\epsilon D(\epsilon) = \frac{V}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \int_0^\infty d\epsilon \epsilon^{1/2} \left(e^{-(\epsilon-\mu)/T} \mp e^{-2(\epsilon-\mu)/T} \right)$$

$$\int_0^\infty d\epsilon \epsilon^{1/2} e^{-\epsilon/T} = T^{3/2} \int_0^\infty dy y^{1/2} e^{-y} \quad \begin{array}{l} \text{Let } y = x^2 \\ dy = 2x dx \end{array}$$

$$= T^{3/2} \int_0^\infty 2x^2 e^{-x^2} = T^{3/2} \frac{\sqrt{\pi}}{2}$$

$$\int_0^\infty d\epsilon \epsilon^{1/2} e^{-2\epsilon/T} = \left(\frac{T}{2} \right)^{3/2} \int_0^\infty dy y^{1/2} e^{-y} = \left(\frac{T}{2} \right)^{3/2} \frac{\sqrt{\pi}}{2}$$

$$\text{Therefore, } n = \frac{N}{V} = \frac{1}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \frac{\sqrt{\pi}}{2} T^{3/2} \left(e^{\mu/T} \mp \frac{1}{2^{3/2}} e^{2\mu/T} \right) + \dots$$

$$= n_Q e^{\mu/T} \left(1 \mp \frac{1}{2^{3/2}} e^{\mu/T} \right) + \dots$$

$$\text{Thus } e^{\mu/T} = \frac{n}{n_Q} + \text{h.o.} \Rightarrow e^{\mu/T} = \frac{n}{n_Q} \left(1 \pm \frac{1}{2^{3/2}} \frac{n}{n_Q} \right) + \dots$$

$$\Rightarrow \mu/T = \ln \frac{n}{n_Q} + \ln \left(1 \pm \frac{1}{2^{3/2}} \frac{n}{n_Q} \right)$$

$$= \ln \frac{n}{n_Q} \pm \frac{1}{2^{3/2}} \frac{n}{n_Q}$$

$$\Rightarrow \mu = T \left(\ln \frac{n}{n_Q} \pm \frac{1}{2^{3/2}} \frac{n}{n_Q} \right) \quad \begin{array}{l} \text{+ Fermi} \\ \text{- Bose} \end{array}$$

$$c) F = \int \mu dN. \quad \text{Since } \int_0^N dN \ln N = N \ln N - N$$

$$\int_0^N dN N = \frac{1}{2} N^2$$

$$F = T \left(\ln \frac{1}{V n_Q} + N \ln N - N \pm \frac{1}{2^{5/2}} \frac{N^2}{V n_Q} \right)$$

$$\Rightarrow F = NT \left(\ln \frac{n}{n_Q} - 1 \pm \frac{1}{2^{5/2}} \frac{n}{n_Q} \right)$$

$$d) \quad p = - \frac{\partial F}{\partial V} = NT \left(\frac{1}{V} \pm \frac{1}{2^{5/2}} \frac{n}{V n_Q} \right)$$

$$\Rightarrow \quad p = \frac{NT}{V} \left(1 \pm \frac{1}{4\sqrt{2}} \frac{n}{n_Q} \right) \quad \begin{array}{l} + \text{ Fermi} \\ - \text{ Bose} \end{array}$$

The first quantum correction makes the pressure larger for fermions and smaller for bosons. That makes sense; fermions want to avoid one another, while bosons want to be together.

2) Fermions in a harmonic potential well

a) Define the zero of energy so that $E_j^0 = j \hbar \omega$.

Suppose in the excited state $E_j = n_j \hbar \omega$ where $n_j \geq j$

$$\text{Then} \quad \frac{E}{\hbar \omega} = n = \sum_{j=1}^N (n_j - j).$$

Here we have expressed n as a sum of nonnegative integers listed in nonascending order — each integer is no larger than the preceding one. That is because $n_j \geq n_{j-1} + 1$ and therefore $(n_j - j) \geq (n_{j-1} - j - 1)$.

The positive integers in the sum provide a partition of n ; furthermore, each partition of n arises in some possible state (assuming $N \geq n$) and no two partitions correspond to the same state. Therefore,

$$g(n) = p(n)$$

$$b) \quad g(n) = p(n) \approx \frac{e^{\pi \sqrt{2n/3}}}{4\sqrt{3}n}$$

$$\Rightarrow \sigma(n) = \ln g(n) = \pi \sqrt{2n/3} + \dots$$

$$\text{and } \frac{1}{T} = \frac{\partial \sigma}{\partial E} = \frac{\partial \sigma}{\partial (k_B n)} = \frac{1}{k_B} \pi \sqrt{\frac{2}{3}} \frac{1}{2} n^{-1/2}$$

$$\Rightarrow T = k_B \frac{\sqrt{6n}}{\pi}$$

$$c) \quad \frac{1}{C} = \frac{\partial T}{\partial E} = \frac{\partial}{\partial n} \left(\frac{\sqrt{6n}}{\pi} \right) = \frac{1}{\pi} \sqrt{\frac{3}{2}} n^{-1/2}$$

$$\Rightarrow C = \pi \sqrt{\frac{2n}{3}} \Rightarrow C = \frac{\pi^2}{3} T / k_B$$

3) Efficiency of a heat engine at peak power

$$a) \quad Q_h = Ktx, \quad Q_c = Kty \Rightarrow$$

$$\text{Work } W = Q_h - Q_c = Kt(x-y) \quad \text{where } x = T_h - T_{hw}$$

$$\text{and cycle takes time } 2t \Rightarrow \quad y = T_{ew} - T_c$$

$$\text{Power} = \frac{\text{Work}}{\text{time}} = \frac{Kt(x-y)}{2t} = \frac{1}{2} K(x-y)$$

$$b) \quad \text{Carnot cycle for working fluid} \Rightarrow$$

$$\frac{Q_h}{T_{hw}} = \frac{Q_c}{T_{ew}} \Rightarrow \frac{Ktx}{T_h - x} = \frac{Kty}{T_c + y}$$

$$\Rightarrow (T_c + y)x = (T_h - x)y \Rightarrow T_c x = (T_h - 2x)y$$

$$\Rightarrow y = \frac{T_c x}{T_h - 2x}$$

$$c) \quad \text{We are to maximize power} \propto x - y = x - \frac{T_c x}{T_h - 2x}$$

$$\Rightarrow \frac{d}{dx} (x - y) = 1 - \frac{T_c}{T_h - 2x} - \frac{2T_c x}{(T_h - 2x)^2} = 0$$

$$\Rightarrow (T_h - 2x)^2 - T_c(T_h - 2x) - 2T_c x = 0$$

$$= 4x^2 + (-4T_h + 2T_c - 2T_c)x + T_h^2 - T_h T_c$$

$$\Rightarrow 0 = x^2 - T_h x + \frac{1}{4}(T_h^2 - T_h T_c)$$

$$\Rightarrow x = \frac{1}{2}(T_h \pm \sqrt{T_h^2 - T_h^2 + T_h T_c})$$

$$= \frac{1}{2}(T_h \pm \sqrt{T_h T_c})$$

$$\text{Therefore } y = \frac{T_c x}{T_h - (T_h \pm \sqrt{T_h T_c})} = \mp \sqrt{\frac{T_c}{T_h}} x.$$

We want the solution with $y > 0 \Rightarrow$

$$x = \frac{1}{2}(T_h - \sqrt{T_h T_c}), \quad y = \frac{1}{2}(\sqrt{T_h T_c} - T_c)$$

$$T_{hw} = T_h - x = \frac{1}{2}(T_h + \sqrt{T_h T_c})$$

$$T_{cw} = T_c + y = \frac{1}{2}(T_c + \sqrt{T_h T_c})$$

d) Efficiency is $\eta = \frac{W}{Q_h} = \frac{Kt(x-y)}{Kt x} = 1 - \frac{y}{x}$

$$\Rightarrow \eta = 1 - \sqrt{\frac{T_c}{T_h}}.$$

Compare with $\eta_c = 1 - \frac{T_c}{T_h}.$

$$\Rightarrow \frac{\eta_c}{\eta} = 1 + \sqrt{\frac{T_c}{T_h}}, \quad \text{which is } > 1 \text{ for } T_c > 0, \text{ and approaches } 2 \text{ as } T_c \rightarrow T_h.$$

Real heat engines have efficiency reasonably close to η .

4) Fun with partial derivatives

$$a) \quad d\epsilon = \left(\frac{\partial \epsilon}{\partial T}\right)_V dT + \left(\frac{\partial \epsilon}{\partial V}\right)_T dV$$

$$\text{and } dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP$$

$$\Rightarrow d\epsilon = \left(\frac{d\epsilon}{dT}\right)_V dT + \left(\frac{\partial \epsilon}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial \epsilon}{\partial V}\right)_T \left(\frac{\partial V}{\partial P}\right)_T dP.$$

Holding P fixed:

$$\left(\frac{\partial \epsilon}{\partial T}\right)_P = \left(\frac{\partial \epsilon}{\partial T}\right)_V + \left(\frac{\partial \epsilon}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$$

b) To eliminate $\left(\frac{\partial \epsilon}{\partial V}\right)_T$ in favor of $\left(\frac{\partial P}{\partial T}\right)_V$,

$$\text{consider } dF = -\epsilon dT - P dV$$

Because $\left(\frac{\partial}{\partial T}\right)_V \left(\frac{\partial}{\partial V}\right)_T$ commute, we have

$$\left(\frac{\partial \epsilon}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \Rightarrow$$

$$C_P - C_V = T \left(\left(\frac{\partial \epsilon}{\partial T}\right)_P - \left(\frac{\partial \epsilon}{\partial T}\right)_V \right) = T \left(\frac{\partial \epsilon}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$$

$$\Rightarrow C_P - C_V = T \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P$$

$$c) \quad dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP = 0 \quad (\text{when } V \text{ fixed})$$

$$\Rightarrow \left(\frac{dP}{dT}\right)_V = - \frac{(\partial V / \partial T)_P}{(\partial V / \partial P)_T}$$

d) Plug (c) into (b):

$$C_P - C_V = -T \frac{(\partial V / \partial T)_P^2}{(\partial V / \partial P)_T}$$

Since $K_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T$, $\beta_P = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P$,

$$C_p - C_v = TV \frac{\beta_P^2}{K_T}.$$