HW#9

9.1

For particle in a cube of volume $V = L^3$, we have $L = \frac{n}{2}\lambda,$ the momentum is

$$p = h/\lambda = n\pi\hbar/L$$

(a) For relativistic ideal gas, we have

$$\varepsilon_n \cong pc = n\pi\hbar c/L$$

$$Z = \sum \exp(-\varepsilon_n/\tau) = \frac{\pi}{2}\int_0^\infty dn n^2 \exp(-\varepsilon_n/\tau) = \frac{\pi}{2}\int_0^\infty dn n^2 \exp(-n\pi\hbar c/L\tau)$$

Let $t = n\pi\hbar c/L\tau$,

$$Z = \frac{\pi}{2}\times(\frac{L\tau}{\pi\hbar c})^3\int_0^\infty dt t^2 \exp(-t) = \text{constant}\times\tau^3$$

Thus

$$U = \tau^2\frac{\partial}{\partial\tau}\ln Z = \tau^2\frac{\partial}{\partial\tau}(3\ln\tau) = 3\tau$$

(b) For nonrelativistic ideal gas, we have

$$\varepsilon_n = \frac{p^2}{2m} = \frac{n^2\pi^2\hbar^2}{2mL^2}$$

$$Z = \sum \exp(-\varepsilon_n/\tau) = \frac{\pi}{2}\int_0^\infty dn n^2 \exp(-\varepsilon_n/\tau) = \frac{\pi}{2}\int_0^\infty dn n^2 \exp(-\frac{n^2\pi^2\hbar^2}{2mL^2\tau})$$

Let $t = \frac{n^2\pi^2\hbar^2}{2mL^2\tau}$,then $dt = \frac{\pi^2\hbar^2}{mL^2\tau}ndn$

$$Z = \frac{\pi}{2}\times\frac{mL^2\tau}{\pi^2\hbar^2}\times(\frac{2mL^2\tau}{\pi^2\hbar^2})^{1/2}\times\int_0^\infty dt t^{1/2}\exp(-t) = \text{constant}\times\tau^{3/2}$$

Thus

$$U = \tau^2\frac{\partial}{\partial\tau}\ln Z = \tau^2\frac{\partial}{\partial\tau}(\frac{3}{2}\ln\tau) = \frac{3}{2}\tau$$

9.2

From (6.32), for ideal gas

$$U = \frac{3}{2}N\tau$$

We can get

$$\left(\frac{\partial U}{\partial\tau}\right)_V = \frac{3}{2}N = C_V, \left(\frac{\partial U}{\partial V}\right)_\tau = 0$$

From (6.29)

$$p = N\tau / V$$

Thus

$$d\sigma = C_V \frac{d\tau}{\tau} + N\frac{dV}{V}$$
$$\Rightarrow \int d\sigma = \int C_V \frac{d\tau}{\tau} + \int N\frac{dV}{V}$$
$$\Rightarrow \sigma = C_V \log\tau + N\log V + \sigma_1$$

Where σ_1 is a constant, independent of τ and V

9.3

(a)

From (6.44), we have

$$Z_{\text{int}} = \sum_{\text{int}} \exp(-\varepsilon_{\text{int}}/\tau) = 1 + \exp(-\Delta/\tau)$$

From (6.48), we can get

$$\mu = \tau[\log(n/n_Q) - \log Z_{\text{int}}] = \tau\{\log(n/n_Q) - \log[1+\exp(-\Delta/\tau)]\}$$

(b)

From (6.24) and (6.49), we have

$$F_{ext} = N\tau[\log(n/n_Q) - 1], F_{\text{int}} = -N\tau\log Z_{\text{int}}$$

Thus,

$$F = F_{ext} + F_{\text{int}} = N\tau[\log(n/n_Q) - 1] - N\tau\log Z_{\text{int}}$$
$$= N\tau\{\log(n/n_Q) - \log[1+\exp(-\Delta/\tau)] - 1\}$$

(c)

From (6.34), we have

$$\sigma_{ext} = N[\log(n_Q/n) + \frac{5}{2}]$$

From (6.50), we can get

$$\sigma_{\text{int}} = -\left(\frac{\partial F_{\text{int}}}{\partial\tau}\right)_V = \frac{\partial}{\partial\tau}(N\tau\log Z_{\text{int}}) = N\log Z_{\text{int}} + N\tau\frac{\partial}{\partial\tau}\log Z_{\text{int}}$$

$$= N\log[1+\exp(-\Delta/\tau)] + N\tau \times \frac{1}{1+\exp(-\Delta/\tau)} \times \exp(-\Delta/\tau) \times \Delta/\tau^2$$

$$= N\log[1+\exp(-\Delta/\tau)] + \frac{N\Delta}{\tau}\frac{\exp(-\Delta/\tau)}{1+\exp(-\Delta/\tau)}$$

$$= N\{\log[1+\exp(-\Delta/\tau)] + \frac{\Delta/\tau}{\exp(\Delta/\tau)+1}\}$$

Thus

$$\sigma = \sigma_{ext} + \sigma_{\text{int}} = N[\log(n_Q / n) + \frac{5}{2}] + N\{\log[1 + \exp(-\Delta/\tau)] + \frac{\Delta/\tau}{\exp(\Delta/\tau) + 1}\}$$

$$= N\{\log(n_Q / n) + \log[1 + \exp(-\Delta/\tau)] + \frac{\Delta/\tau}{\exp(\Delta/\tau) + 1} + \frac{5}{2}\}$$

(d)

From (6.28)

$$p = -\left(\frac{\partial F}{\partial V}\right)_{\tau,N} = -\left(\frac{\partial F_{\text{int}}}{\partial V}\right)_{\tau,N} - \left(\frac{\partial F_{ext}}{\partial V}\right)_{\tau,N}$$

For

$$F_{\text{int}} = \log[1 + \exp(-\Delta/\tau)]\}$$

$$\Rightarrow \left(\frac{\partial F_{\text{int}}}{\partial V}\right)_{\tau,N} = 0$$

From (6.29), we can get

$$p = -\left(\frac{\partial F_{ext}}{\partial V}\right)_{\tau,N} = \frac{N\tau}{V}$$

(e)

From (6.37)

$$C_p = \tau\left(\frac{\partial \sigma}{\partial \tau}\right)_p = \tau\left(\frac{\partial \sigma_{ext}}{\partial \tau}\right)_p + \tau\left(\frac{\partial \sigma_{\text{int}}}{\partial \tau}\right)_p$$

From (38c)

$$C_{ext} = \tau\left(\frac{\partial \sigma_{ext}}{\partial \tau}\right)_p = \frac{5}{2}N$$

$$C_{\text{int}} = \tau\left(\frac{\partial \sigma_{\text{int}}}{\partial \tau}\right)_p = N\tau\frac{\partial}{\partial \tau}\{\log[1 + \exp(-\Delta/\tau)] + \frac{\Delta/\tau}{\exp(\Delta/\tau) + 1}\}$$

$$= N\tau\{\frac{\exp(-\Delta/\tau)}{1 + \exp(-\Delta/\tau)} \times \Delta/\tau^2 + \frac{-\Delta/\tau^2 \times [\exp(\Delta/\tau) + 1] - \Delta/\tau \times \exp(\Delta/\tau) \times (-\Delta/\tau^2)}{[\exp(\Delta/\tau) + 1]^2}\}$$

$$= \frac{N\Delta^2}{\tau^2}\frac{\exp(\Delta/\tau)}{[\exp(\Delta/\tau) + 1]^2}$$

$$C_p = C_{ext} + C_{\text{int}} = \frac{N\Delta^2}{\tau^2}\frac{\exp(\Delta/\tau)}{[\exp(\Delta/\tau) + 1]^2} + \frac{5}{2}N$$

9.4

(a)

From (5.53), the Gibbs sum is

$$Z = \sum_N \sum_S \exp[(N\mu - \varepsilon_s)/\tau] = \sum_N \lambda^N \sum_S \exp(-\varepsilon_s/\tau) = \sum_N \lambda^N Z_N$$
$$= \sum_N \lambda^N (n_Q V)^N / N! = \sum_N (\lambda n_Q V)^N / N! = \exp(\lambda n_Q V)$$

(b)

$$P(N) = \frac{(\lambda n_Q V)^N / N!}{Z} = \frac{(\lambda n_Q V)^N / N!}{\exp(\lambda n_Q V)} = <N>^N \exp(-<N>)/N!$$

Where $<N> = \lambda n_Q V$

(c)

$$\sum_N P(N) = \exp(-<N>)\sum_N <N>^N / N!$$
$$= \exp(-<N>)\exp(<N>) = 1$$

$$\sum_N NP(N) = N\exp(-<N>)\sum_N <N>^N / N!$$
$$= <N> \exp(-<N>)\sum_N <N>^{N-1} / (N-1)!$$
$$= <N> \exp(-<N>)\exp(<N>)$$
$$= <N>$$