Homework-8. Problems: 3, 5, 6, 12, 14, 15 in chapter 6

6.3) DISTRIBUTION FUNCTION FOR DOUBLE OCCUPANCY STATISTICS

(a) Occupancy: 0 1 2

Energy : 0 ε 2ε

$$\mathcal{Z}_{DO} = 1 + \lambda e^{-\varepsilon/\tau} + \lambda^2 e^{-2\varepsilon/\tau}$$

$$\langle N\rangle_{DO} = \frac{1}{\mathcal{Z}}\left[0 + \lambda e^{-\varepsilon/\tau} + 2\lambda^2 e^{-2\varepsilon/\tau}\right] .$$

(b) Occupancy: 0,0 0,1 1,0 1,1

Energy : 0 ε ε 2ε

$$\mathcal{Z} = 1 + 2\lambda e^{-\varepsilon/\tau} + \lambda^2 e^{-2\varepsilon\tau}$$

$$= [1+\lambda e^{-\varepsilon/\tau}]^2;$$

$$\langle N\rangle = \frac{1}{\mathcal{Z}}\left[0 + 2\lambda e^{-\varepsilon/\tau} + 2\lambda^2 e^{-2\varepsilon/\tau}\right] .$$

The last line may be written

$$\langle N\rangle = 2\lambda e^{-\varepsilon/\tau}\ \frac{1+\lambda e^{-\varepsilon/\tau}}{[1+\lambda e^{-\varepsilon/\tau}]^2} = \frac{2}{\exp[(\varepsilon-\mu)/\tau]+1} .$$

The Gibbs sum is square of a single-orbital Gibbs sum, as one would expect for two independent single-orbital systems. See Problem 3.9 for comparison. The occupancy is just twice the Fermi-Dirac distribution function.

6.5) INTEGRATION OF THERMODYNAMIC IDENTITY FOR AN IDEAL GAS

From $U = 3N\tau/2$:

$$(\partial U/\partial \tau)_V = 3N/2 = C_V, \quad (\partial U/\partial V)_\tau = 0 \quad .$$

If these and $p = n\tau/V$ are inserted into (75):

$$d\sigma = C_V d\tau/\tau + NdV/V = C_V d(\log \tau) + N\, d(\log V) \quad ;$$

$$\sigma = C_V \log \tau + N \log V + \text{constant}. \tag{76}$$

6.6) ENTROPY OF MIXING

For a single gas of N atoms with the concentration $n = N/V$, from (34):

$$\sigma = N[\log(n_Q/n) + 5/2] \quad .$$

For two distinguishable independent gases, each state of gas A may be combined with each state of gas B to generate a distinct state of the combined system. If g_A and g_B are the numbers of states accessible to each gas, $g = g_A g_B$ is the number of states accessible to the two-gas system, and the two-gas entropy is the sum of the one-gas entropies: $\sigma = \sigma_A + \sigma_B$.

This is true both before and after diffusive contact. Before contact, each of the two concentrations is $n = n_i = N/V$, hence

$$\sigma_i = N[\log(n_{QA}/n_i) + \log(n_{QB}/n_i) + 5] \quad ,$$

where n_{QA} and n_{QB} will in general be different. After diffusive equilibrium, $n = n_f = N/2V = n_i/2$; therefore

$$
\begin{aligned}
\sigma_f &= N[\log(n_{QA}/n_f) + \log(n_{QB}/n_f) + 5] \\
&= N[\log(2n_{QA}/n_i) + \log(2n_{QB}/n_i) + 5] \\
&= \sigma_i + 2N \log 2 \quad .
\end{aligned}
$$

The additional term 2N log 2 may be understood as follows. For every A-atom orbital in volume V_A there is an equivalent A-atom orbital in V_B, and for every B-atom orbital in V_B there is an equivalent B-atom orbital in V_A. States in which these equivalent orbitals are occupied are initially inaccessible, but they become accessible upon diffusive contact. Every accessible state of the two-gas system with diffusive contact may be viewed as having been generated from one of the initially accessible states by interchanging the occupancies of an arbitrary number (from 0 to 2N) of equivalent orbital pairs. For 2N occupied orbitals, there are 2^{2N} distinguishable combinations of interchanges, leading to 2^{2N} distinguishable accessible states for every initially accessible state. The entropy of mixing is the logarithm of this multiplicity of mixing: $\sigma_M = \log 2^{2N} = 2N \log 2$.

If the particles are indistinguishable, these occupancy interchanges do not lead to new distinguishable states but merely re-arrange the accessible states amongst each other. The two gases in diffusive contact are then simply a single gas of 2N atoms with the unchanged concentration $n_f = 2N/2V = n_i$, and with the entropy

$$\sigma_f = 2N[\log(n_Q/n_i) + 5/2] \quad .$$

For indistinguishable gases $n_{QA} = n_{QB}$; therefore $\sigma_f = \sigma_i$.

Comment. Students often ask whether particles can be "nearly" identical. The answer is: no! Particles differ either by a finite discrete amount or not at all. For example, the different isotopes of an element differ in the (discrete) number of neutrons in their nuclei.

6.12) IDEAL GAS IN TWO DIMENSIONS

(a) Analogously to (3.59) and to (15),

$$\varepsilon_n = \frac{\hbar^2}{2M}\left(\frac{\pi}{L}\right)^2 (n_x{}^2 + n_y{}^2) = \frac{\hbar^2\pi^2}{2MA} n^2 \quad , \quad n^2 = n_x{}^2 + n_y{}^2 ,$$

$$N = \sum f(\varepsilon_n) = \lambda \sum \exp(-\varepsilon_n/\tau) \quad .$$

The sum goes over $n_x > 0$ and $n_y > 0$ independently. We replace the sum by an integral

$$\sum \ldots = (\pi/2) \int_0^\infty \ldots\ ndn \quad .$$

If we substitute variables according to $x = \varepsilon_n/\tau = (\hbar^2\pi^2/2MA\tau)n^2$, $dx = (\hbar^2\pi^2/MA\tau)ndn$, we obtain

$$N = \lambda\frac{\pi}{2}\,\frac{MA\tau}{\hbar^2\pi^2}\int_0^\infty \exp(-x)dx = \lambda A n_Q{}^* \quad ,$$

where

$$n_Q{}^* = M\tau/2\pi\hbar^2 \qquad \text{(S1)}$$

is the two-dimensional quantum concentration. Next:

$$\mu = \tau \log \lambda = \tau \log (n^*/n_Q{}^*) \quad , \quad n^* = N/A \quad , \qquad \text{(S2)}$$

the same result as (18) in 3 dimensions, except for the replacement of n and n_Q by n^* and $n_Q{}^*$.

(b) $$U = \sum \varepsilon_n f(\varepsilon_n) = \lambda \sum \varepsilon_n \exp(-\varepsilon_n/\tau)$$

$$= \lambda\tau^2 \frac{\partial}{\partial\tau}\sum \exp(-\varepsilon_n/\tau)$$

$$= \lambda A\tau^2(\partial n_Q{}^*/\partial\tau) = \lambda A n_Q{}^*\tau = N\tau \quad .$$

(c) We noted that μ in (S2) had the same form as for a three-dimensional gas, except for the substitutions $n \to n^*$, $n_Q \to n_Q{}^*$. We may therefore obtain F as in (22) and (23):

$$F = N\tau[\log(n^*/n_Q{}^*) - 1] \quad .$$

From this, (33) and (S1)

$$\sigma = -(\partial F/\partial \tau)_{A,N} = -N[\log(n^*/n_Q{}^*) - 1] - N\tau$$
$$= N[\log(n_Q{}^*/n^*) + 2] \quad .$$

6.13) GIBBS SUM FOR IDEAL GAS

(a) $$\mathcal{Z} = \sum_{ASN} \exp[(N\mu - \varepsilon_s)/\tau] = \sum_N \lambda^N \sum_s \exp(-\varepsilon_s/\tau)$$
$$= \sum_N \lambda^N Z_N = \sum_N (\lambda n_Q V)^N/N! = \exp(\lambda n_Q V) \quad .$$

(b) $$P(N) = (\lambda n_Q V)^N/(N!\mathcal{Z}) = (\lambda n_Q V)^N \exp[-(\lambda n_Q V)]/N!$$
$$= \langle N\rangle^N \exp(-\langle N\rangle)/N! \ , \quad \text{with } \langle N\rangle = \lambda n_Q V \quad .$$

(c) $$\sum P(N) = \exp(-\langle N\rangle)\sum \langle N\rangle^N/N! = \exp(-\langle N\rangle)\exp\langle N\rangle = 1 \quad .$$
$$NP(N) = \langle N\rangle[\langle N\rangle^{N-1}/(N-1)!]\exp(-\langle N\rangle) = \langle N\rangle P(N-1) \quad ;$$
$$\sum_{N=0} NP(N) = \sum_{N=1} NP(N) = \langle N\rangle \sum_{N=1} P(N-1) = \langle N\rangle \quad .$$

6.14) IDEAL GAS CALCULATIONS

(a) The heat added during the isothermal expansion is

$$Q = -W = \int_{V_1}^{2V_1} p\,dV = N\tau \int_{V_1}^{2V_1} dV/V = N\tau \log 2$$
$$= Nk_B \times 300 \text{ K} \times \log 2 = 1{,}729 \text{ J} \quad .$$

There is no heat added during the isentropic expansion.

(b) From (66),

$$T_2(4V_1)^{\gamma-1} = T_1(2V_1)^{\gamma-1} \ ; \ T_2 = T_1 \times (1/2)^{\gamma-1} \quad .$$

For a monatomic ideal gas $\gamma = 5/3$ and $\gamma-1 = 2/3$, hence

$$T_2 = 300\ K/2^{2/3} = 189\ K \quad .$$

(c) From (34), with $n_2 = n_1/2$

$$\Delta S = k_B \Delta\sigma = Nk_B[\log(n_Q/n_2) - \log(n_Q/n_1)]$$

$$= Nk_B \log 2 = 5.76\ J\ K^{-1} \quad .$$

6.15) DIESEL ENGINE COMPRESSION

From (66):

$$T_2 V_2^{\gamma-1} = T_1 V_1^{\gamma-1} \quad ,$$

$$T_2 = T_1 \times (V_1/V_2)^{\gamma-1} = 300\ K \times 15^{0.4} = 886\ K = 613°C.$$