Solutions to exercises week 45

FYS2160

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Schroeder 5.23

a)

Writing $\Phi = U - TS - \mu N$ in terms of infinitesimal changes of the quantities involved:

$$d\Phi = dU - TdS - SdT - \mu dN - Nd\mu.$$

Inserting the thermodynamic identity for dU gives

$$d\Phi = -PdV - SdT - Nd\mu.$$

The partial derivatives of Φ wrt. T, V or μ is obtained by holding the two other quantities fixed:

$$\left(\frac{\partial \Phi}{\partial T}\right)_{V,\mu} = -S, \qquad \left(\frac{\partial \Phi}{\partial V}\right)_{T,\mu} = -P, \qquad \left(\frac{\partial \Phi}{\partial \mu}\right)_{T,V} = -N.$$

b)

As was done for F and G in chapter 5.2 in Schroeder, express an infinitesimal change in the total entropy S_{total} as a sum of changes in the entropy S of the

system and the entropy S_R of the reservoir it is in contact with:

$$dS_{\text{total}} = dS + dS_R.$$

Assuming V fixed, apply the thermodynamic identity to dS_R (solve the expression for dU_R in terms of dS_R), and use the fact that $dU_R = -dU$ and $dN_R = -dN$ to write dS_R in terms of system variables. The total entropy of the system plus reservoir (expressed in terms of system variables) is then

$$dS_{\text{total}} = -\frac{1}{T}(dU - TdS - \mu dN) = -\frac{1}{T}d\Phi.$$

The tendency of the total entropy to increase therefore means that the grand free energy tends to decrease (since dS_{total} is positive, $d\Phi$ must be negative in order to make $-d\Phi/T$ positive).

c)

$$\Phi = U - TS - \mu N$$
$$= U - TS + PV - PV - \mu N$$
$$= G - PV - \mu N$$
$$= -PV,$$

where we in the last step use that $G = \mu N$ when T and P are constant (from the thermodynamic identity of G, $dG = -SdT + VdP + \mu dN$ with $dN = 1$).

d)

For the unoccupied state: $U = S = N = 0 \Rightarrow \Phi = 0$.

For the occupied state: $U = U_0 = -13.6$ eV, $S = 0$, $N = 1$

$$\Phi_{\text{occupied}} = U_0 - \mu$$

$$= U_0 + kT \ln\left[\frac{V}{N}\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right],$$

where eq. 3.63 in Schroeder is used for the chemical potential of an ideal gas. Here m is the electron mass, and the electron concentration is given as $N/V = 2 \times 10^{19}$ m^{-3}. Putting in numbers gives us (the logarithm is calculated to be equal to 17.8)

$$\Phi_{\text{occupied}} = -13.6 \text{ eV} + 8.62 \times 10^{-5} \text{ eV/K} \times 5800 \text{ K} \times 17.8$$

$$\approx -4.7 \text{ eV} < \Phi_{\text{unoccupied}} = 0 \text{ eV}.$$

To find the temperature at which the occupied and unoccupied states are equally likely, we set their grand free energies to be equal and solve for T (neglecting the $\ln T^{3/2}$ dependence, which is insignificant compared to the factor T outside the logarithm, when T is varied):

$$\Phi_{\text{occupied}} = \Phi_{\text{unoccupied}}$$

$$U_0 - 17.8kT = 0$$

$$T = -\frac{U_0}{17.8k} \approx 8800 \text{ K}$$

Schroeder 7.1

Probability of heme site being occupied:

$\mathcal{P} = \frac{1}{e^{(\epsilon - \mu)/kT} + 1}$

Blood in equilibrium with air, that we can view as an ideal gas, giving the chemical potential:

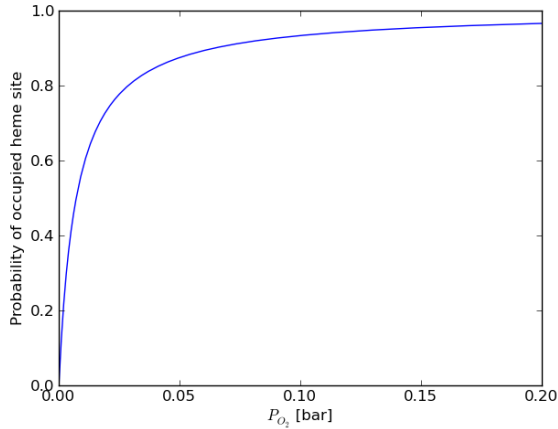$\mu = -kT \ln\left(\frac{V Z_{\text{int}}}{N v_Q}\right) = -kT \ln\left(\frac{kT Z_{\text{int}}}{P v_Q}\right),$

where P is the partial pressure.

From this we get

$$\mathcal{P} = \frac{1}{e^{\epsilon/kT}\frac{kTZ_{\text{int}}}{Pv_Q}+1} = \frac{1}{\frac{P_0}{P}+1},$$

where $P_0 = e^{\epsilon/kT}\frac{kTZ_{\text{int}}}{v_Q}$.

T = 310K, kT = 0.0267 eV, ϵ = -0.7 eV, P_0 = 0.0072 bar

Schroeder 7.7

Grand potential/free energy:

$$\Phi = U - TS - \mu N$$

Grand partition function:

$$\mathcal{Z} = \sum_s e^{-[E(s)-\mu N(s)]/kT}$$

From exercise 5.23 we have

$$\left(\frac{\partial \Phi}{\partial \mu}\right)_{T,V} = -N.$$

For a $\tilde{\Phi} = -kT\ln\mathcal{Z}$ we get

$$\left(\frac{\partial \tilde{\Phi}}{\partial \mu}\right)_{T,V} = -\bar{N}.$$

So Φ and $\tilde{\Phi}$ obeys the same differential equation.

We set an initial value $\mu = 0$, then $\Phi = U - TS = F$ and $\mathcal{Z} = Z$ (the ordinary partition function). So for $\mu = 0$, $\tilde{\Phi} = -kT\ln\mathcal{Z} = -kT\ln Z = F = \Phi$, where we use $F = -kT\ln Z$ from section 6.5.

Φ and $\tilde{\Phi}$ obeys the same differential equation and and are the same at the initial condition $\mu = 0$, therefore they must be the same function, giving us: $\Phi = \tilde{\Phi} = -kT \ln \mathcal{Z}$.

Schroeder 7.14

From Figure 7.7 the distributions more or less coincide for $\epsilon - \mu$ a few times greater than kT. This gives:

$\frac{\bar{n}_{\text{BE}}}{\bar{n}_{\text{FD}}} = \frac{e^{(\epsilon-\mu)/kT}+1}{e^{(\epsilon-\mu)/kT}-1} = \frac{1+e^{-(\epsilon-\mu)/kT}}{1-e^{-(\epsilon-\mu)/kT}} \approx 1 + 2e^{-(\epsilon-\mu)/kT}$, for $(\epsilon - \mu)/kT \gg 1$

For a 1% difference between $\bar{n}_{\text{BE}}$ and $\bar{n}_{\text{FD}}$ (Boltzmann distribution lies between BE and FD distributions (Boltzmann distribution lies between BE and FD distributions) we require:

$2e^{-(\epsilon-\mu)/kT} < 0.01 \Rightarrow \frac{(\epsilon-\mu)}{kT} > \ln(200) \approx 5.3$

For particles at room temperature T = 300K we get:

$(\epsilon - \mu) > 0.137$ eV.

For an ordinary gas of particles in a box, energy levels measured in the usual way ϵ is positive and $-\mu/kT$ is $\ln(V Z_{\text{int}}/N v_Q)$.

The condition above is then:

$\frac{V Z_{\text{int}}}{N v_Q} = \frac{kT Z_{\text{int}}}{P v_Q} > 200$

For nitrogen at room temperature and atmospheric pressure:

$\frac{kT Z_{\text{int}}}{P v_Q} = 3.0 \times 10^8$,

which is easily satisfied.

Schroeder 7.15

Total number of particles:

$N = \sum_s \bar{n}_{\text{Boltzmann}} = \sum_s = e^{-(\epsilon_s - \mu)/kT} = e^{\mu/kT} \sum_s e^{-\epsilon_s/kT}$

Single-particle partition function:

$$Z_1 = \sum_s = e^{-\epsilon_s/kT}$$
This gives:
$$N = Z_1 e^{\mu/kT} \Rightarrow \mu = -kT \ln\left(\frac{Z_1}{N}\right)$$

Schroeder 7.20

For an electron gas at the centre of the sun we have the Fermi temperature:
$$T_F = \frac{\epsilon_F}{k} = \frac{h^2}{8mk}\left(\frac{3N}{\pi V}\right)^{2/3} = 9.1 \times 10^6 K$$
This temperature is close to the actual temperature in the sun, $T = 10^7$ K, so we can not threat the electron gas as a degenerate Fermi gas ($T \approx 0$) or an ordinary "classical" ideal gas ($T \gg T_F$).

Schroeder 7.26

a)

The Fermi energy is:
$$\epsilon_F = \frac{h^2}{8m}\left(\frac{3N}{\pi V}\right)^{2/3} \approx 6.9 \times 10^{-23} J \approx 4.3 \times 10^{-4} eV,$$
with $N/V = N_A/(37\text{cm}^3)$ where N_A is the Avogadro number.

b)

From equation 7.48 we have:
$$\frac{C_V}{NkT} = \frac{\pi^2 k}{2\epsilon_F} = \frac{\pi^2}{2T_F} \approx 1.0 K^{-1}$$
The predicted heat capacity is smaller by almost a factor of 3.

c)

Entropy of liquid ^{3}He:
$$S = \int_0^T \frac{C_V}{T'} dT' = (2.8 K^{-1})Nk \int_0^T dT' = (2.8 K^{-1})NkT$$
Entropy of solid ^{3}He: $S = k\ln(2^N) = Nk\ln 2$,

this applies for temperatures down to low values before it freeze out and goes to 0.

Same entropy for:

$Nk \ln 2 = (2.8K^{-1})NkT \Rightarrow T = \frac{\ln 2}{2.8K^{-1}} = 0.25K$

By Clausius-Clapeyron relation the slope of the solid-liquid phase boundary on the PT graph is proportional to the entropy difference $S_{\text{liquid}-S_{\text{solid}}}$. We predict the slope to be negative at temperatures lower than 0.25 K and positive for temperatures greater than 0.25 K. We see this behaviour in Figure 5.13.