Physics 12c, Problem Set 6 Solutions

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[1] Thermal ionization of hydrogen (Pr. 9.2 of Kittel/Kroemer)

(a) We can directly apply Eq. (9.35) of Kittel and Kroemer,

$$\prod_j n_j^{\nu_j} = K(\tau), \tag{1.1}$$

with $n_1 = [e]$, $\nu_1 = 1$, $n_2 = [H^+]$, $\nu_2 = 1$, and $n_3 = [H]$, $\nu_3 = -1$. Then $K(\tau)$ is given by Eq. (9.34),

$$K(\tau) = \prod_j n_{Q\ j}{}^{\nu_j} \exp[-\nu_j F_j/\tau] = \frac{n_{Q\ e} n_{Q\ H^+}}{n_{Q\ H}} \exp[(F_H - F_e - F_{H^+})/\tau]. \tag{1.2}$$

However, $n_{Q\ H^+} \approx n_{Q\ H}$ since their mass is nearly the same, so using $I = F_H - F_e - F_{H^+}$ for the energy required to ionize hydrogen we find that $K(\tau) \approx n_{Q\ e} \exp[-I/\tau]$, so

$$[e][H^+]/[H] \approx n_{Q\ e} \exp[-I/\tau]. \tag{1.3}$$

If $[e] = [H^+]$, this equation can be solved for $[e]$ to yield

$$[e] \approx [H]^{1/2} n_Q^{1/2} \exp[-I/(2\tau)]. \tag{1.4}$$

(b) The relative concentration of $H(exc)$ follows from the standard Boltzmann factor argument:

$$\frac{[H(exc)]}{H} = 4 \exp\left[-\frac{3}{4}\frac{I}{\tau}\right]. \tag{1.5}$$

where the factor of 4 comes from the degeneracy of the first excited state of hydrogen atom (n=2).

The ionization energy of hydrogen is 13.6 eV. On the surface of the Sun, $\tau \approx 0.43$ eV, and $n_Q \approx 8.4 \times 10^{20}$ cm^{-3}.

Hence, while $[H(exc)] \approx 2.08 \times 10^{13}$ cm^{-3}, we find that $[e] \approx 1.3 \times 10^{15}$ cm^{-3}.

[2] Particle-antiparticle equilibrium (Pr. 9.5 of Kittel/Kroemer)

(a) With $\nu^+ = \nu^- = 1$ and $n^+ = n^- = n$, the law of mass action gives

$$n^+ n^- = n^2 = n_Q^2 \exp\left(-\frac{F_{\text{int}}^+ + F_{\text{int}}^-}{\tau}\right),$$

where n_Q is the same for both species since they have the same mass (assumed spinless). The energy released when A$^+$ annihilates with A$^-$ has a minimum Δ when both particles are at rest so that the energy released just comes from their internal (free) energy. Therefore, $\Delta = F_{\text{int}}^+ + F_{\text{int}}^-$, and we have

$$n = n_Q \exp\left(-\frac{\Delta}{2\tau}\right), \tag{2.1}$$

(b) For the electron (no internal structure), ignoring spin, the quantum concentration is

$$n_Q = \left(\frac{m_e \tau}{2\pi\hbar^2}\right)^{3/2} \approx 1.27 \times 10^{19} \text{cm}^{-3},$$

for $T = 300$K. Assume $n_{e^-} = n_{\text{hole}} = n$, and $\Delta/\tau = 20$. Then,

$$n = n_Q \exp\left(-\frac{1}{2}\frac{\Delta}{\tau}\right) \approx 5.8 \times 10^{14} \text{cm}^{-3}. \tag{2.2}$$

(c) For a particle of spin s, the spin contribution to the internal partition function is $Z_{\text{int}} = 2s + 1$, which is the number of independent spin states. For spin $\frac{1}{2}$, $Z_{\text{int}} = 2$. Assuming that Δ is a measured quantity so that spin contributions are already included, the only thing we need to correct for is the quantum concentration $n_Q \to Z_{\text{int}} n_Q = 2n_Q$, where n_Q as usual is for the monatomic, spinless particle. Therefore, the answer from part (a) becomes:

$$n = 2n_Q \exp\left(-\frac{\Delta}{2\tau}\right). \tag{2.3}$$

[3] Latent Heat of melting

$$C_A = N\alpha\tau^3; C_b = N\beta\tau \tag{3.1}$$

(a)

$$\sigma(\tau) = \sigma(0) + \int_0^\tau C_P/\tau d\tau. \tag{3.2}$$

So,

$$\sigma_A = \frac{1}{3}N\alpha\tau^3, \sigma_B = N\beta\tau \tag{3.3}$$

(b)

$$U(\tau) = N\epsilon_0 + \int_0^\tau C d\tau. \tag{3.4}$$

So,

$$U_A = \frac{1}{4}N\alpha\tau^4 + N\epsilon_0, U_B = \frac{1}{2}N\beta\tau^2 + N\epsilon_0 \tag{3.5}$$

(c)

$$\mu = \left(\frac{\partial U}{\partial N}\right)_\sigma \tag{3.6}$$

So,

$$U_A = N\epsilon_0 + \frac{1}{4}N\alpha\left(\frac{3\sigma_A}{N\alpha}\right)^{4/3} \to \mu_A = \epsilon_0 - \frac{1}{3N}(U_A - N\epsilon_0) = \epsilon_0 - \frac{1}{12}\alpha\tau^4. \tag{3.7}$$

And,

$$U_B = N\epsilon_0 + \frac{1}{2}N\beta\left(\frac{\sigma_B}{N\beta}\right)^2 \to \mu_B = \epsilon_0 - \frac{1}{N}(U_B - N\epsilon_0) = \epsilon_0 - \frac{1}{2}\beta\tau^2. \tag{3.8}$$

(d) Since $\mu_B < \mu_A$ for small τ, B is favored at low temperature. At transition, $\mu_A = \mu_B$. So,

$$\tau_m^2 = \frac{6B}{\alpha} \tag{3.9}$$

(e)

$$L = \tau_m \Delta\sigma = \frac{1}{3}N\alpha\tau_m^4 - N\beta\tau_m^2 = 6N\beta^2/\alpha \tag{3.10}$$

[4] Latent Heat of BEC

Bose-Einstein condensation of an ideal gas may be regarded as a sort of first-order phase transition, where the two coexisting phases are the "liquefied" condensate (the particles in the ground orbital) and the "normal" gas (the particles in excited orbitals). The purpose of this problem is to calculate the latent heat of this transition. Assume that the particles are spinless bosons with mass m. For this problem you may express your answers in terms of the function

$$I(\alpha) = \int_0^\infty dx\ \frac{x^\alpha}{e^x - 1}.$$

(a) As for an nonrelativistic ideal gas in the classical regime, the pressure P of a bosonic ideal gas is related to its internal energy U and volume V by $P = \frac{2}{3}\frac{U}{V}$ even when the temperature τ is below the Einstein condensation temperature τ_E. Why?

In a cubic box with side L, the orbital labeled by integers n_x, n_y, n_z has energy

$$E(n_x, n_y, n_z) = \frac{\hbar^2\pi^2}{2mL^2}\left(n_x^2 + n_y^2 + n_z^2\right).$$

So for fixed n_x, n_y, n_z, the energy scales like $V^{-2/3}$, where V is the volume of the box, and therefore

$$\frac{\partial}{\partial V}E(n_x, n_y, n_z) = -\frac{2}{3}V^{-1}E(n_x, n_y, n_z)$$

In an isolated system (constant entropy), the pressure is

$$P = -\left\langle \frac{\partial E}{\partial V} \right\rangle = \frac{2}{3}\frac{U}{V}.$$

(*b*) *For a fixed particle number $N \gg 1$ and a nonzero temperature τ, the gas is uncondensed when its volume is large enough. But as the gas is compressed at constant temperature, Bose-Einstein condensation occurs at some critical concentration n^*. Find this critical concentration.*

When condensation occurs the chemical potential μ vanishes, and the number of particles in excited orbitals matches the total number of particles:

$$\begin{aligned} n^* = \frac{N}{V^*} &= \int_0^\infty d\epsilon\ \mathcal{D}(\epsilon)\frac{1}{e^{\epsilon/\tau}-1} \\ &= \frac{1}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\int_0^\infty d\epsilon\ \frac{\epsilon^{1/2}}{e^{\epsilon/\tau}-1} \\ &= \frac{1}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\tau^{3/2}\ I\left(1/2\right). \end{aligned} \tag{4.11}$$

(*c*) *As we continue to compress the gas at constant temperature beyond the condensation concentration, the pressure remains constant as more and more of the gas liquefies. Find this coexistence pressure $P_{\text{coex}}(\tau)$.*

The pressure is $P = \frac{2}{3}\frac{U}{V}$, where

$$\begin{aligned} U/V &= \int_0^\infty d\epsilon\ \mathcal{D}(\epsilon)\frac{\epsilon}{e^{\epsilon/\tau}-1} \\ &= \frac{1}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\int_0^\infty d\epsilon\ \frac{\epsilon^{3/2}}{e^{\epsilon/\tau}-1} \\ &= \frac{1}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\tau^{5/2}\ I\left(3/2\right). \end{aligned} \tag{4.12}$$

(*d*) *Condensation continues until all particles are in the ground orbital, which occurs at essentially zero volume if the temperature is nonzero. Use the Clausius-Clapeyron relation to express the latent heat L of the transition in terms of the temperature τ. (The latent heat is the amount of heat released during the liquefication of the gas at temperature τ.)*

The latent heat is

$$L = \tau\Delta v\left(\frac{dP}{d\tau}\right)_{\text{coex}},$$

where $\Delta v = v^* = (n^*)^{-1}$. From (*c*) we have

$$\left(\frac{dP}{d\tau}\right)_{\text{coex}} = \frac{5}{2}\frac{P}{\tau} = \frac{5}{3\tau}\frac{U}{V};$$

therefore,

$$L = \frac{5}{3}\frac{U/V}{n^*} = \frac{5}{3}\frac{I(3/2)\tau^{5/2}}{I(1/2)\tau^{3/2}} = 1.284\ \tau.$$

(*e*) *Now check your expression for L by computing it another way. Calculate the work done as the gas is compressed from concentration n^* to zero volume, and calculate how the internal energy U changes as the gas is compressed. Use the first law to find the latent heat L.*

The work done during compression is

$$W = P\Delta V = \frac{2}{3}\frac{U}{V}\Delta V = \frac{2}{3}N\frac{U/V}{n^*} = \frac{2}{3}N\tau\frac{I(3/2)}{I(1/2)}.$$

The change in the internal energy is

$$\Delta U = -\frac{U}{V}\Delta V = -N\tau\frac{I(3/2)}{I(1/2}.$$

The heat *released* as the gas "liquefies" is

$$-Q = -\Delta U + W = \left(1 + \frac{2}{3}\right) N\tau\frac{I(3/2)}{I(1/2};$$

hence the latent heat per particle is $L = \frac{5}{3}\tau\frac{I(3/2)}{I(1/2}$, in agreement with ($d$).

[5] Boiling water on Mount Everest

a) *The boiling temperature τ_0 of water at sea level is such that its vapor pressure matches the atmospheric pressure P_0. At what temperature τ_1 would water boil if the atmospheric pressure were P_1 instead? Treat the water vapor as a classical ideal gas, and assume that the latent heat of vaporization per particle L is independent of temperature. Also assume that the volume per particle in liquid water is negligible compared to the volume per particle in water vapor.*

According to the Clausius-Clapeyron relation,

$$\left(\frac{dP}{d\tau}\right)_{\text{coex}} = \frac{L}{\tau\Delta v},$$

and

$$\Delta v = v_g - v_l \approx v_g = \tau/P,$$

by the ideal gas law; hence

$$\left(\frac{dP}{d\tau}\right)_{\text{coex}} = \frac{L}{\tau^2}P.$$

Integrating along the coexistence curve, we find that coexistence pressure and temperature are related by

$$\ln(P_1/P_0) = L\left(-\frac{1}{\tau_1} + \frac{1}{\tau_0}\right),$$

or

$$\frac{1}{\tau_1} = \frac{1}{\tau_0} + \frac{1}{L}\ln(P_0/P_1).$$

b) Suppose that the atmosphere is an isothermal ideal gas of molecular nitrogen at 300°*K. Find the boiling temperature of water at the top of Mount Everest. The latent heat of vaporization of water is 41 kJ per mole, and Mount Everest is 8.8 km high.*

For an atmosphere in thermal and diffusive equilibrium at temperature $\bar{\tau}$, the chemical potential is independent of the altitude h, hence the pressure varies with h as

$$P_h = P_0 e^{-mgh/\bar{\tau}},$$

or

$$\ln(P_0/P_h) = mgh/\bar{\tau},$$

and therefore (using part (a))

$$\frac{1}{\tau_h} = \frac{1}{\tau_0} + \frac{1}{\bar{\tau}}\frac{mgh}{L}.$$

The molecular weight of N_2 is 28 (28 g per mole), so

$$\frac{mgh}{L} = \frac{(.028)(9.8)(8800)}{41,000} \approx .059.$$

Using $\bar{\tau} = 300°\mathrm{K}$ and $\tau_0 = 373°\mathrm{K}$ (the boiling temperature of water at sea level), we obtain

$$\frac{1}{\tau_h} = \frac{1}{373} + \frac{.059}{300},$$

or

$$\tau_h = 348°\mathrm{K} = 75°\mathrm{C}.$$