

PHYSICS 112
Homework 4 Solutions

1. The specific heat, per unit volume of a crystal at low temperature is given by

$$\frac{C_{\text{phonon}}}{k_B} = \frac{12\pi^4 n}{5} \left(\frac{T}{\theta_D} \right)^3 ,$$

while the specific heat per unit volume of a photon gas is

$$\frac{C_{\text{photon}}}{k_B} = \frac{4\pi^2}{15(\hbar c)^3} (k_B T)^3 ,$$

which can be obtained by differentiating the energy density in Eq. (20), Ch. 4 of the book with respect to T . Taking the ratio gives

$$\frac{C_{\text{phonon}}}{C_{\text{photon}}} = 9\pi^2 n \left(\frac{\hbar c}{k_B \theta_D} \right)^3 \left(\frac{T_{\text{phonon}}}{T_{\text{photon}}} \right)^3 , \quad (1)$$

where we have allowed different temperatures for the photons and phonons.

[*Note:* Since θ_D is defined by

$$k_B \theta_D = \hbar v (6\pi^2 n)^{1/3}$$

where v is the sound speed, (see Eqs. (42) and (43) of the book), Eq. (1) is equivalent to

$$\frac{C_{\text{phonon}}}{C_{\text{photon}}} = \frac{3}{2} \left(\frac{c}{v} \right)^3 \left(\frac{T_{\text{phonon}}}{T_{\text{photon}}} \right)^3 . \quad (2)$$

This is mentioned in the question.]

Setting the specific heats in Eq. (1) to be equal gives

$$T_{\text{photon}} = (9\pi^2 n)^{1/3} \frac{\hbar c}{k_B \theta_D} T_{\text{phonon}} .$$

Putting $T_{\text{phonon}} = 1 \text{ K}$ and $n = 10^{22} \text{ cm}^{-3}$ gives

$$T_{\text{photon}} = \frac{(9 \times 3.142^2 \times 10^{22})^{1/3} \times 1.055 \times 10^{-27} \times 3 \times 10^{10}}{1.38 \times 10^{-16} \times 100} \simeq \boxed{2.2 \times 10^5 \text{ K}} .$$

As shown in Eq. (2), the ratio of temperatures, 2.2×10^5 , is the ratio of the speed of light to the speed of sound (apart from a factor $(3/2)^{1/3}$).

2. Consider a column of gas in the atmosphere of unit cross sectional area. We showed in class that the density varies with height h as

$$n(h) = n_0 \exp(-mgh/k_B T) ,$$

where n_0 is the density at $h = 0$.

- (a) The number of atoms in the column whose height is between h and $h + dh$ is $n(h) dh$. Their contribution to the potential energy is $mgh n(h) dh$. Hence the *average* potential energy per atom is obtained by integrating this over h and dividing by the total number of atoms in the column, i.e.

$$\langle \text{PE} \rangle = \frac{mg n_0 \int_0^\infty h \exp(-mgh/k_B T) dh}{n_0 \int_0^\infty \exp(-mgh/k_B T) dh} = \boxed{k_B T},$$

where to get the final answer we let $x = mgh/k_B T$ and used the following integrals:

$$\int_0^\infty \exp(-x) dx = 1, \quad \int_0^\infty x \exp(-x) dx = 1.$$

- (b) To get the specific heat we need the contribution from both the potential energy and kinetic energy. The kinetic energy per atom is $3k_B T/2$ (we are assuming that T is independent of h), see Eq. (65) of Ch. 3 of Kittel and Kroemer, which gives a specific heat of $3k_B/2$, while the above result for the potential energy gives a specific heat per atom of k_B . Adding them together gives a total specific heat per atom of

$$\boxed{C = \frac{5}{2} k_B}.$$

3. (a) There are three possible states:

(A) no particle: this gives a contribution of 1 to \mathcal{Z}

(B) one particle in a state of zero energy: contribution is $\exp(\beta\mu)$

(C) one particle in state with energy ϵ : contribution is $\exp(\beta\mu - \beta\epsilon)$.

Adding up gives

$$\boxed{\mathcal{Z} = 1 + \lambda + \lambda \exp(-\beta\epsilon)},$$

where λ , which is known as the activity, is equal to $\exp(\beta\mu)$.

- (b) The probabilities of the system being in states A, B, and C are:

$$P_A = \frac{1}{\mathcal{Z}}, \quad P_B = \frac{\lambda}{\mathcal{Z}}, \quad P_C = \frac{\lambda \exp(-\beta\epsilon)}{\mathcal{Z}},$$

and so the expectation value of the number of particles is given by

$$\langle N \rangle = 0 \cdot P_A + 1 \cdot P_B + 1 \cdot P_C = \boxed{\frac{\lambda + \lambda \exp(-\beta\epsilon)}{\mathcal{Z}}}.$$

- (c) The average occupancy of the state at energy ϵ is P_C which is equal to

$$\boxed{\frac{\lambda \exp(-\beta\epsilon)}{\mathcal{Z}}}.$$

- (d) The average energy is given by

$$U = 0 \cdot P_A + 0 \cdot P_B + \epsilon \cdot P_C = \boxed{\frac{\epsilon \lambda \exp(-\beta\epsilon)}{\mathcal{Z}}}.$$

(e) Now we add a fourth state, D, with two particles and energy ϵ , and so

$$\mathcal{Z} = 1 + \lambda + \lambda \exp(-\beta\epsilon) + \lambda^2 \exp(-\beta\epsilon) = (1 + \lambda) [1 + \lambda \exp(-\beta\epsilon)] .$$

Because \mathcal{Z} can be factored, the states with energy zero and energy ϵ are effectively two independent systems.

4. There are four states as specified in the question. Weighting them according to the Gibbs distribution, the average number of electrons is

$$\frac{\lambda [\exp(\beta\Delta/2) + \exp(-\beta\Delta/2)] + 2\lambda^2 \exp(-\beta\delta/2)}{\exp(\beta\delta/2) + \lambda [\exp(\beta\Delta/2) + \exp(-\beta\Delta/2)] + \lambda^2 \exp(-\beta\delta/2)} ,$$

where $\beta = 1/\tau$. Setting this (rather complicated) expression equal to unity gives the desired condition, i.e.

$$\lambda [\exp(\beta\Delta/2) + \exp(-\beta\Delta/2)] + 2\lambda^2 \exp(-\beta\delta/2) = \exp(\beta\delta/2) + \lambda [\exp(\beta\Delta/2) + \exp(-\beta\Delta/2)] + \lambda^2 \exp(-\beta\delta/2)$$

and simplifying gives

$$\lambda^2 \exp(-\beta\delta/2) = \exp(\beta\delta/2) , \quad (3)$$

which corresponds to the probability of there being two electrons is equal to the probability of their being no electrons. (This condition is equivalent to the average being one.) Eq. (3) can be written as

$$\lambda^2 = \exp(\beta\delta) ,$$

as desired.

5. There are three possible states:

(0) Site is vacant: energy = 0.

(A) O_2 molecule: energy = ϵ_A

(B) CO molecule: energy = ϵ_B

The corresponding weights in the Gibbs distribution are

$$(0) \ 1, \quad (A) \ \lambda(O_2) \exp(-\beta\epsilon_A), \quad (B) \ \lambda(CO) \exp(-\beta\epsilon_B) .$$

- (a) Assume there is no CO, i.e. $\lambda(CO) = 0$. The probability that an O_2 molecule is attached is therefore

$$\frac{\lambda(O_2) \exp(-\beta\epsilon_A)}{1 + \lambda(O_2) \exp(-\beta\epsilon_A)} .$$

For this to equal 0.9 we need

$$\lambda(O_2) \exp(-\beta\epsilon_A) = 9 . \quad (4)$$

and putting in $\lambda(O_2) = 1 \times 10^{-5}$ gives

$$\epsilon_A = k_B T \ln(10^{-5}/9) = \boxed{-0.37\text{ev}} .$$

where we used $T = 37^\circ \text{C} = 310 \text{K}$, and $1 \text{ev} = 1.6 \times 10^{-19} \text{J}$.

- (b) Now allow for contamination by CO. The probability that the site is occupied by an O_2 molecule is now

$$\frac{\lambda(O_2) \exp(-\beta\epsilon_A)}{1 + \lambda(O_2) \exp(-\beta\epsilon_A) + \lambda(CO) \exp(-\beta\epsilon_B)},$$

where we are given $\lambda(CO) = 1 \times 10^{-7}$. For this to be reduced to 0.1 one has, using Eq. (4),

$$0.1 = \frac{9}{1 + 9 + 10^{-7} \exp(-\beta\epsilon_B)},$$

which gives

$$\epsilon_B = \boxed{-0.55\text{ev.}}$$

6. (a)

$$\langle N \rangle = \frac{1}{\mathcal{Z}} \left\{ \sum_N N \sum_l \exp[\beta(N\mu - E_l)] \right\} = \frac{k_B T}{\mathcal{Z}} \left(\frac{\partial \mathcal{Z}}{\partial \mu} \right)_{T,V} = - \left(\frac{\partial \Omega}{\partial \mu} \right)_{T,V}, \quad (5)$$

where Ω , the grand potential, is equal to $-k_B T \ln \mathcal{Z}$.

- (b) Similarly

$$\langle N^2 \rangle = \frac{1}{\mathcal{Z}} \left\{ \sum_N N^2 \sum_l \exp[\beta(N\mu - E_l)] \right\} = \frac{(k_B T)^2}{\mathcal{Z}} \left(\frac{\partial^2 \mathcal{Z}}{\partial \mu^2} \right)_{T,V},$$

and hence

$$\langle (\Delta N)^2 \rangle \equiv \langle N^2 \rangle - \langle N \rangle^2 = (k_B T)^2 \left[\frac{1}{\mathcal{Z}} \left(\frac{\partial^2 \mathcal{Z}}{\partial \mu^2} \right) - \frac{1}{\mathcal{Z}^2} \left(\frac{\partial \mathcal{Z}}{\partial \mu} \right)^2 \right].$$

- (c) Differentiating Eq. (5) with respect to μ , and noting that one has to differentiate both $\partial \mathcal{Z} / \partial \mu$ and the factor of \mathcal{Z} in the denominator, we get

$$\frac{\partial \langle N \rangle}{\partial \mu} = k_B T \left\{ \frac{1}{\mathcal{Z}} \left(\frac{\partial^2 \mathcal{Z}}{\partial \mu^2} \right) - \frac{1}{\mathcal{Z}^2} \left(\frac{\partial \mathcal{Z}}{\partial \mu} \right)^2 \right\} = \boxed{\frac{1}{k_B T} \langle (\Delta N)^2 \rangle},$$

where we used part (a) in the last equality.

Note: The left hand side is of order N and so the size of typical fluctuations in N , which is given by $\langle (\Delta N)^2 \rangle^{1/2}$, is of order \sqrt{N} which is much less than N if N is very large. Hence, as stated in class, *relative* fluctuations in N are small, in the Gibbs distribution, for a large system.

7. We are given that the density of water vapor at the bottom is n_0 and the density in the air at the leaves is equal to $0.9n_0$. In order for the water vapor to rise in the tree to the leaves, the density of water vapor in the pores of the tree must exceed that in the outside air at the leaves, $0.9n_0$. We showed in class that the density varies with h as

$$n(h) = n_0 \exp(-mgh/k_B T),$$

and so we need

$$n_0 \exp(-mgh/k_B T) > 0.9n_0,$$

or

$$\frac{mgh}{k_B T} < \ln(1/0.9) = 0.105.$$

This gives

$$h < 0.105 \frac{k_B T}{mg}.$$

Putting in $T = 25^\circ\text{C} = 298\text{K}$, $g = 9.81\text{ms}^{-2}$, $m = 18 \times 1.67 \times 10^{-27}\text{kg}$, and $k_B = 1.38 \times 10^{-23}\text{JK}^{-1}$, (where we have noted that the mass of a water molecule is essentially 18 times that of a proton whose mass is given in the back of the book), we get the maximum height to be

$$\frac{0.105 \times 1.38 \times 10^{-23} \times 298}{18 \times 1.67 \times 10^{-27} \times 9.81} \simeq \boxed{1460\text{m}.}$$