

1. Consider a system that may be unoccupied with zero energy or occupied by one particle in either of two states, one of energy zero and one of energy  $\varepsilon_0$ .

(a) Show that the grand partition function for this system is

$$Z = 1 + \lambda + \lambda e^{-\varepsilon_0/kT}$$

Our assumption excludes the possibility of one particle in each state at the same time. Notice that we include a term for  $N = 0$  as a particular state of the system of a variable number of particles.

(b) Show that the thermal average occupancy of the system is

$$\langle N \rangle = \frac{\lambda + \lambda e^{-\varepsilon_0/kT}}{Z}$$

(c) Show that the thermal average occupancy of the state at energy  $\varepsilon_0$  is

$$\langle N(\varepsilon_0) \rangle = \frac{\lambda e^{-\varepsilon_0/kT}}{Z}$$

(d) Find an expression for the thermal average energy of the system.

(e) Allow the possibility that the orbital at 0 and at  $\varepsilon_0$  may be occupied each by one particle at the same time; show that

$$Z = 1 + \lambda + \lambda e^{-\varepsilon_0/kT} + \lambda^2 e^{-\varepsilon_0/kT} = (1 + \lambda) \left[ 1 + \lambda e^{-\varepsilon_0/kT} \right]$$

Because  $Z$  can be factored as shown, we have in effect two independent systems.

(a) There are three possible combinations of states and numbers, ( $N = 0, \varepsilon = 0$ ), ( $N = 1, \varepsilon = 0$ ), and ( $N = 1, \varepsilon = \varepsilon_0$ ). Using these in the grand partition function:

$$Z = \sum_{ASN} \lambda^N e^{-\varepsilon/kT} = 1 + \lambda + \lambda e^{-\varepsilon_0/kT}$$

(b) Here, we can just do the sum:

$$\langle N \rangle = \sum_{ASN} N \frac{\lambda^N e^{-\varepsilon/kT}}{Z} = (0) \frac{\lambda^0 e^{-0/kT}}{Z} + (1) \frac{\lambda^1 e^{-0/kT}}{Z} + (1) \frac{\lambda^1 e^{-\varepsilon_0/kT}}{Z} = \frac{\lambda(1 + e^{-\varepsilon_0/kT})}{Z}$$

(c) We can just do the sum again:

$$\langle N(\varepsilon_0) \rangle = \sum_{ASN} N(\varepsilon_0) \frac{\lambda^N e^{-\varepsilon/kT}}{Z} = (0) \frac{\lambda^0 e^{-0/kT}}{Z} + (0) \frac{\lambda^1 e^{-0/kT}}{Z} + (1) \frac{\lambda^1 e^{-\varepsilon_0/kT}}{Z} = \frac{\lambda e^{-\varepsilon_0/kT}}{Z}$$

(d) This is almost identical to the previous answer:

$$\langle \varepsilon \rangle = \sum_{ASN} \varepsilon \frac{\lambda^N e^{-\varepsilon/kT}}{Z} = (0) \frac{\lambda^0 e^{-0/kT}}{Z} + (0) \frac{\lambda^1 e^{-0/kT}}{Z} + (\varepsilon_0) \frac{\lambda^1 e^{-\varepsilon_0/kT}}{Z} = \frac{\varepsilon_0 \lambda e^{-\varepsilon_0/kT}}{Z}$$

(e) Since the two states can be occupied independently, we have another choice in our sum, ( $N = 2, \varepsilon = \varepsilon_0$ ), so the grand partition function is now

$$Z = \sum_{ASN} \lambda^N e^{-\varepsilon/kT} = 1 + \lambda + \lambda e^{-\varepsilon_0/kT} + \lambda^2 e^{-\varepsilon_0/kT} = (1 + \lambda) \left( 1 + \lambda e^{-\varepsilon_0/kT} \right)$$

2. *Carbon monoxide poisoning.* In carbon monoxide poisoning the CO replaces the O<sub>2</sub> adsorbed on hemoglobin (Hb) molecules in the blood. To show the effect, consider a model for which each adsorption site on a heme may be vacant or may be occupied either with energy  $\varepsilon_A$  by one O<sub>2</sub> molecule or with energy  $\varepsilon_B$  by one CO molecule. Let  $N$  fixed heme sites be in equilibrium with O<sub>2</sub> and CO in the gas phase at concentrations such that the activities are  $\lambda(\text{O}_2) = 1 \times 10^{-5}$  and  $\lambda(\text{CO}) = 1 \times 10^{-7}$ , all at body temperature 37°C. Neglect any spin multiplicity factors.

- (a) First consider the system in the absence of CO. Evaluate  $\varepsilon_A$  such that 90% of the Hb sites are occupied by O<sub>2</sub>. Express the answer in eV per O<sub>2</sub>.  
 (b) Now admit the CO under the specified conditions. Find  $\varepsilon_B$  such that only 10% of the Hb sites are occupied by O<sub>2</sub>.

(a) We want the occupancy to be 90%. That requires a certain energy,  $\varepsilon_A$ . First I'll express  $kT$  in terms of eV,  $kT = (1.38 \times 10^{-23} \text{ J/K}) (310 \text{ K}) (1 \text{ eV}/1.6 \times 10^{-19} \text{ J}) = 0.0267 \text{ eV}$ .

$$Z = \sum_{\text{ASN}} \lambda^N e^{-\varepsilon/kT} = 1 + \lambda e^{-\varepsilon_A/kT}$$

$$\langle N \rangle = \sum_{\text{ASN}} N \frac{\lambda^N e^{-\varepsilon/kT}}{Z} = \frac{\lambda e^{-\varepsilon_A/kT}}{1 + \lambda e^{-\varepsilon_A/kT}}$$

We can solve this last equation for  $\varepsilon_A$ :

$$(1 + \lambda e^{-\varepsilon_A/kT}) \langle N \rangle = \lambda e^{-\varepsilon_A/kT}$$

$$e^{\varepsilon_A/kT} + \lambda = \frac{\lambda}{\langle N \rangle}$$

$$e^{\varepsilon_A/kT} = \lambda \left( \frac{1}{\langle N \rangle} - 1 \right)$$

$$\varepsilon_A = kT \ln \left[ \lambda \left( \frac{1}{\langle N \rangle} - 1 \right) \right]$$

Plugging in the numbers:

$$\varepsilon_A = (0.0267 \text{ eV}) \ln \left[ (1 \times 10^{-5}) \left( \frac{1}{0.9} - 1 \right) \right] = -0.37 \text{ eV}$$

(b) Now we have two different activities and different occupation possibilities:

$$Z = \sum_{\text{ASN}} \lambda^N e^{-\varepsilon/kT} = 1 + \lambda(\text{O}_2) e^{-\varepsilon_A/kT} + \lambda(\text{CO}) e^{-\varepsilon_B/kT}$$

$$\langle N \rangle(\text{O}_2) = \sum_{\text{ASN}} N(\text{O}_2) \frac{\lambda^N e^{-\varepsilon/kT}}{Z} = \frac{\lambda(\text{O}_2) e^{-\varepsilon_A/kT}}{1 + \lambda(\text{O}_2) e^{-\varepsilon_A/kT} + \lambda(\text{CO}) e^{-\varepsilon_B/kT}}$$

We can now solve the above equation for  $\varepsilon_B$ :

$$1 + \lambda(\text{O}_2) e^{-\varepsilon_A/kT} + \lambda(\text{CO}) e^{-\varepsilon_B/kT} = \frac{\lambda(\text{O}_2) e^{-\varepsilon_A/kT}}{\langle N \rangle(\text{O}_2)}$$

$$e^{-\varepsilon_B/kT} = \frac{1}{\lambda(\text{CO})} \left[ \lambda(\text{O}_2) e^{-\varepsilon_A/kT} \left( \frac{1}{\langle N \rangle(\text{O}_2)} - 1 \right) - 1 \right]$$

$$\varepsilon_B = -kT \ln \left[ \frac{\lambda(\text{O}_2) e^{-\varepsilon_A/kT}}{\lambda(\text{CO})} \left( \frac{1}{\langle N \rangle(\text{O}_2)} - 1 \right) - \frac{1}{\lambda(\text{CO})} \right]$$

Plugging in the numbers:

$$\varepsilon_B = - (0.0267 \text{ eV}) \ln \left[ \frac{10^{-5} e^{0.37 \text{ eV}/0.0267 \text{ eV}}}{10^{-7}} \left( \frac{1}{.1} - 1 \right) - 10^7 \right] = -0.55 \text{ eV}$$

The state with CO occupancy has a lower energy than the O<sub>2</sub> occupancy.

3. Baierlein 8.1. *Another meaning for  $\langle n_\alpha \rangle_F$ .*

(a) For fermions, construct a proof that

$$\left( \begin{array}{c} \text{probability that single-particle} \\ \text{state } \phi_\alpha \text{ is occupied} \end{array} \right) = \langle n_\alpha \rangle_F$$

Start with the probability  $P(\Psi_j)$  or at least use them. This result extends the significance of  $\langle n_\alpha \rangle_F$  from merely “the estimated number of particles in  $\phi_\alpha$ .”

(b) Why does such a result *not* hold for bosons?

(a) To find the probability that a given single-particle state is occupied, we sum over all of the probabilities  $P(\Psi_j)$  in which that state is occupied.

$$P(\text{state } \phi_\alpha \text{ occ.}) = \sum_{\substack{\text{all } j \text{ in which} \\ \phi_\alpha \text{ is occupied}}} P(\Psi_j)$$

Since  $n_\alpha = 1$  for all of these states, we can write this as

$$P(\text{state } \phi_\alpha \text{ occ.}) = \sum_{\substack{\text{all } j \text{ in which} \\ \phi_\alpha \text{ is occupied}}} n_\alpha P(\Psi_j)$$

and since  $n_\alpha = 0$  for all the states not included in the sum, we can extend this over all states,

$$P(\text{state } \phi_\alpha \text{ occ.}) = \sum_j n_\alpha P(\Psi_j) = \langle n_\alpha \rangle$$

(b) This only applies to fermions where the occupation number is 0 or 1. This does not apply to bosons where the occupation number can be greater than 1.

4. Baierlein 8.2. *Some effects of spin.*

(a) Use the limiting expression in section 8.4, specifically relations (8.18) to (8.22), to compute the energy, pressure, and chemical potential of an  $N$ -particle gas in terms of  $T$ ,  $V$ , and  $N$ . Specify that each particle has a spin  $s\hbar$ , where  $s$  may differ from 0 and  $\frac{1}{2}$ .

(b) In which calculated quantities does the value of  $s$  make a numerical difference (in this limiting regime)?

(a) The chemical potential is set from

$$N = \sum_\alpha \langle n_\alpha \rangle = \sum_\alpha \varepsilon e^{-(\varepsilon - \mu)/kT}$$

We can use the density of states to do this sum as an integral over the energies, taking into account there will be an extra factor of  $2s + 1$  possible states for each energy due to the possible spin states.

$$N = (2s + 1) \int_0^\infty D(\varepsilon) e^{-(\varepsilon - \mu)/kT} d\varepsilon$$

where  $D(\varepsilon) = 2\pi (2m/h^2)^{3/2} V \varepsilon^{1/2}$ . Note that you can also include the factor of  $2s + 1$  directly in the density of states but do not count this factor twice.

$$N = 2\pi (2s + 1) \left( \frac{2m}{h^2} \right)^{3/2} V e^{\mu/kT} \int_0^\infty \varepsilon^{1/2} e^{-\varepsilon/kT} d\varepsilon$$

Let  $x^2 = \varepsilon/kT$  and  $2x dx = d\varepsilon/kT$ , giving us

$$N = 2\pi (2s + 1) \left(\frac{2m}{h^2}\right)^{3/2} V e^{\mu/kT} (kT)^{3/2} \int_0^\infty 2x^2 e^{-x^2} dx$$

The integral can be looked up or done on Maple,  $\int_0^\infty x^2 e^{-x^2} dx = \sqrt{\pi}/4$ . The equation for the chemical potential is

$$\frac{N}{V} = (2s + 1) \left(\frac{2m\pi kT}{h^2}\right)^{3/2} e^{\mu/kT}$$

The second term in the brackets is related to the thermal deBroglie wavelength,  $\lambda_{th} = h/\sqrt{2\pi mkT}$ . Solving for  $\mu$ :

$$\frac{N}{V} = (2s + 1) \lambda^{-3} e^{\mu/kT} \quad \rightarrow \quad e^{\mu/kT} = \frac{N\lambda^3}{(2s + 1)V}$$

$$\mu = kT \ln \left[ \frac{N\lambda^3}{(2s + 1)V} \right]$$

The chemical potential decreases with  $s$ .

The average energy is

$$\langle E \rangle = \sum_{\alpha} \varepsilon \langle n_{\alpha} \rangle = \sum_{\alpha} \varepsilon e^{-(\varepsilon - \mu)/kT} = e^{\mu/kT} \sum_{\alpha} \varepsilon e^{-\varepsilon/kT}$$

Again, we can use the density of states to do this sum as an integral over the energies. I'll also plug in for the chemical potential.

$$\begin{aligned} \langle E \rangle &= \frac{N\lambda^3}{(2s + 1)V} (2s + 1) \int_0^\infty D(\varepsilon) \varepsilon e^{-\varepsilon/kT} d\varepsilon \\ &= \frac{N\lambda^3}{V} 2\pi \left(\frac{2m}{h^2}\right)^{3/2} V \int_0^\infty \varepsilon^{3/2} e^{-\varepsilon/kT} d\varepsilon \end{aligned}$$

Let  $x^2 = \varepsilon/kT$  and  $2x dx = d\varepsilon/kT$ , giving us

$$\langle E \rangle = 2\pi N\lambda^3 \left(\frac{2m}{h^2}\right)^{3/2} (kT)^{5/2} \int_0^\infty 2x^4 e^{-x^2} dx$$

The integral is  $\int_0^\infty x^4 e^{-x^2} dx = 3\sqrt{\pi}/8$  which gives us

$$\langle E \rangle = 4\pi N\lambda^3 \left(\frac{2m}{h^2}\right)^{3/2} (kT)^{5/2} \frac{3\sqrt{\pi}}{8} = \frac{3}{2} N\lambda^3 \left(\frac{2m\pi kT}{h^2}\right)^{3/2} kT = \frac{3}{2} NkT$$

The average energy is independent of  $s$ .

The Helmholtz free energy is

$$F = \int_0^N \mu dN = \int_0^N kT \ln \left[ \frac{N\lambda^3}{(2s + 1)V} \right] dN = NkT \left\{ \ln \left[ \frac{N\lambda^3}{(2s + 1)V} \right] - 1 \right\}$$

The problem did not ask for this but it is easy to calculate the pressure from the free energy:

$$P = - \left( \frac{\partial F}{\partial V} \right)_{N,T} = \frac{NkT}{V}$$

So the pressure is independent of  $s$  as well.

(b) The average internal energy and the pressure are independent of  $s$  while the chemical potential decreases with  $s$ .

5. Baierlein 8.3. *Criterion for the classical limit.*

- (a) If equations (8.18) to (8.22) are to be self-consistent, what strong inequality must hold among the quantities  $N$ ,  $V$ ,  $m$ , and  $T$ ?  
 (b) What can you say about the sign and size of the chemical potential?

(a) For the classical limit to hold, we must have

$$e^{(\varepsilon - \mu)/kT} \gg 1$$

If this is true we can ignore the 1 relative to this term in the Fermi-Dirac or Bose-Einstein distributions. This is most restrictive for the ground state energy (i.e., the lowest  $\varepsilon$ ). Setting this energy to 0, we have

$$e^{-\mu/kT} \gg 1 \quad \rightarrow \quad \frac{-\mu}{kT} \gg 1$$

Plugging in from the previous problem for  $\mu$ :

$$-\ln \left[ \frac{N\lambda^3}{(2s+1)V} \right] \gg 1 \quad \rightarrow \quad \ln \left[ \frac{(2s+1)V}{N\lambda^3} \right] \gg 1 \quad \rightarrow \quad \frac{(2s+1)V}{N\lambda^3} \gg 1$$

The number of particles in a volume the size of the thermal deBroglie wavelength cubed must be small.

$$\frac{N}{V} \ll (2s+1) \left( \frac{h^2}{2\pi mkT} \right)^{3/2}$$

This requires low density or high temperature.

(b) From above, we have

$$-\mu \gg kT$$

So the chemical potential must be negative and much larger in magnitude than  $kT$ .

6. Baierlein 8.6. *Entropy.* The entropy  $S$  of a quantum ideal gas can be expressed in terms of the estimated occupation numbers:

$$\frac{S}{k} = \sum_{\alpha} [\mp (1 \mp \langle n_{\alpha} \rangle) \ln(1 \mp \langle n_{\alpha} \rangle) - \langle n_{\alpha} \rangle \ln \langle n_{\alpha} \rangle],$$

where the upper sign applies for fermions and the lower for bosons.

- (a) In general, how should the derivative  $(\partial S / \partial T)_V$  be related to the derivative  $(\partial \langle E \rangle / \partial T)_V$ ?  
 (b) Check whether the expression for  $S$  displayed above satisfies the relationship in (a). (Your steps reverse the process by which  $S$  was computed by integration—and are much easier steps.)

(a) At constant volume and number of particles, we have

$$d \langle E \rangle = T dS \quad \rightarrow \quad \left( \frac{\partial \langle E \rangle}{\partial T} \right)_{V,N} = T \left( \frac{\partial S}{\partial T} \right)_{V,N}$$

(b) I'll use  $f = \langle n_{\alpha} \rangle$ . First, let us simplify the expression for  $S$ :

$$\frac{S}{k} = \sum_{\alpha} [\mp (1 \mp f) \ln(1 \mp f) - f \ln f]$$

Take a derivative with respect to  $T$ :

$$\left( \frac{\partial S}{\partial T} \right)_{V,N} = \sum_{\alpha} \left[ f' \ln(1 \mp f) + \frac{\mp (1 \mp f)(\mp f')}{1 \mp f} - f' \ln f - f' \right] = \sum_{\alpha} f' \ln \left( \frac{1 \mp f}{f} \right)$$

where  $f' = (\partial f / \partial T)_{V,N}$ . We know

$$f = \frac{1}{e^{(\varepsilon-\mu)/kT} \pm 1} \quad 1 \mp f = \frac{e^{(\varepsilon-\mu)/kT} \pm 1}{e^{(\varepsilon-\mu)/kT} \pm 1} \mp \frac{1}{e^{(\varepsilon-\mu)/kT} \pm 1} = \frac{e^{(\varepsilon-\mu)/kT}}{e^{(\varepsilon-\mu)/kT} \pm 1} = e^{(\varepsilon-\mu)/kT} f$$

And thus

$$\frac{1 \mp f}{f} = e^{(\varepsilon-\mu)/kT} \quad \rightarrow \quad \ln\left(\frac{1 \mp f}{f}\right) = \frac{(\varepsilon - \mu)}{kT}$$

This gives us

$$\left(\frac{\partial S}{\partial T} \frac{1}{k}\right)_{V,N} = \sum_{\alpha} \frac{(\varepsilon - \mu)}{kT} \left(\frac{\partial f}{\partial T}\right)_{V,N}$$

We can pull the  $1/kT$  out of the sum and we can also pull the  $\mu$  out of the sum (but not the  $\varepsilon$ !) which gives us

$$\left(\frac{\partial S}{\partial T} \frac{1}{k}\right)_{V,N} = \frac{1}{kT} \sum_{\alpha} \varepsilon \left(\frac{\partial f}{\partial T}\right)_{V,N} - \frac{\mu}{kT} \sum_{\alpha} \left(\frac{\partial f}{\partial T}\right)_{V,N}$$

We can now pull the derivative out of the sum:

$$\begin{aligned} \left(\frac{\partial S}{\partial T} \frac{1}{k}\right)_{V,N} &= \frac{1}{kT} \left(\frac{\partial}{\partial T} \sum_{\alpha} \varepsilon f\right)_{V,N} - \frac{\mu}{kT} \left(\frac{\partial}{\partial T} \sum_{\alpha} f\right)_{V,N} \\ &= \frac{1}{kT} \left(\frac{\partial \langle E \rangle}{\partial T}\right)_{V,N} - \frac{\mu}{kT} \left(\frac{\partial N}{\partial T}\right)_{V,N} \end{aligned}$$

The last term is clearly zero. This gives us

$$T \left(\frac{\partial S}{\partial T}\right)_{V,N} = \left(\frac{\partial \langle E \rangle}{\partial T}\right)_{V,N}$$