

August 30, 2007

**Chem. 1410**

**Problem Set 1**, due Sept. 10, 2007

Do the following problems from Engel; these are *not* to be handed in for grading; solutions will be distributed via .pdf.

Chapter 1: P1.2, P1.7, P1.12, P1.17, P1.19

The following two problems are to be handing in for grading:

(1) **Density of states of electromagnetic modes in a blackbody cavity:** In class we asserted that at absolute temperature  $T$  the density of electromagnetic states (“modes”) inside a blackbody is

$$D_{\lambda}(\lambda) = \frac{8\pi}{\lambda^4} \quad [1]$$

(Note: the units of  $D_{\lambda}(\lambda)$  are “# modes/[unit volume][unit wavelength]”.) This means that in a small wavelength interval  $[\lambda - \Delta\lambda/2, \lambda + \Delta\lambda/2]$ , the number of electromagnetic modes per unit volume is  $D_{\lambda}(\lambda)\Delta\lambda$ . Show that Eq. [1] is equivalent to the following density of states in frequency space:

$$D_{\nu}(\nu) = 8\pi\nu^2 / c^3 \quad [2]$$

where  $c$  is the speed of light. (Note: the units of  $D_{\nu}(\nu)$  are “# modes/[unit volume][unit frequency]”.)

The following remarks may be of use:

i)  $\nu = c / \lambda$ .

ii)  $D_{\lambda}(\lambda)\Delta\lambda = D_{\nu}(\nu)\Delta\nu$ , where  $\Delta\lambda$  is a small wavelength interval and  $\Delta\nu$  is the corresponding small frequency interval. [Why?]

Note: Eq. [2] is employed directly in Engel Eq. 1.1.

2) **Average thermal energy in a harmonic oscillator.** According to the principles of statistical physics, the relative probability to find a system in state  $j$  characterized by energy  $E_j$  is  $\exp(-E_j / k_B T)$ , where  $T$  is the absolute temperature and  $k_B$  is Boltzmann's constant.

a) In the case where the system is an electromagnetic cavity mode frequency  $\nu$ , the allowed states  $j=0,1,2,\dots$  correspond to energy  $E_j = jh\nu$  (i.e.,  $0,1,2,\dots$  photons in the mode). Thus, the average thermal energy of a cavity mode of frequency  $\nu$  at absolute temperature  $T$  is given by:

$$\langle E(\nu) \rangle = h\nu \frac{\sum_{j=0}^{\infty} j e^{-jh\nu / k_B T}}{\sum_{j=0}^{\infty} e^{-jh\nu / k_B T}} .$$

Why?

b) To evaluate  $\langle E \rangle$  explicitly, write  $\langle E(\nu) \rangle = h\nu N(\nu) / D(\nu)$ , with

$$N(\nu) = \sum_{j=0}^{\infty} j e^{-jh\nu / k_B T} ; \quad D(\nu) = \sum_{j=0}^{\infty} e^{-jh\nu / k_B T}$$

i) Show that:

$$D(\nu) = [1 - e^{-h\nu / k_B T}]^{-1}$$

[Hint:  $D$  is a simple geometric series.]

ii) Show that

$$N(\nu) = \frac{-k_B T}{h} \frac{\partial D(\nu)}{\partial \nu}$$

iii) Combine the results of i) and ii) to obtain Eq. 1.5 of Engel.