

**PHYSICS 140A : STATISTICAL PHYSICS**  
**HW ASSIGNMENT #1 SOLUTIONS**

(1) The *information entropy* of a distribution  $\{p_n\}$  is defined as  $S = -\sum_n p_n \log_2 p_n$ , where  $n$  ranges over all possible configurations of a given physical system and  $p_n$  is the probability of the state  $|n\rangle$ . If there are  $\Omega$  possible states and each state is equally likely, then  $S = \log_2 \Omega$ , which is the usual dimensionless entropy in units of  $\ln 2$ .

Consider a normal deck of 52 distinct playing cards. A new deck always is prepared in the same order (A♠ 2♠ ⋯ K♣).

- (a) What is the information entropy of the distribution of new decks?
- (b) What is the information entropy of a distribution of completely randomized decks?

Now consider what it means to shuffle the cards. In an ideal *riffle shuffle*, the deck is split and divided into two equal halves of 26 cards each. One then chooses at random whether to take a card from either half, until one runs through all the cards and a new order is established (see figure).



Figure 1: The riffle shuffle.

- (c) What is the increase in information entropy for a distribution of new decks that each have been shuffled once?
- (d) Assuming each subsequent shuffle results in the same entropy increase (*i.e.* neglecting redundancies), how many shuffles are necessary in order to completely randomize a deck?
- (e) If in parts (b), (c), and (d), you were to use Stirling's approximation,

$$K! \sim K^K e^{-K} \sqrt{2\pi K},$$

how would your answers have differed?

**Solution :**

(a) Since each new deck arrives in the same order, we have  $p_1 = 1$  while  $p_{2,\dots,52!} = 0$ . Therefore  $S = 0$ .

(b) For completely randomized decks,  $p_n = 1/\Omega$  with  $n \in \{1, \dots, \Omega\}$  and  $\Omega = 52!$ , the total number of possible configurations. Thus,  $S_{\text{random}} = \log_2 52! = 225.581$ .

(c) After one riffle shuffle, there are  $\Omega = \binom{52}{26}$  possible configurations. If all such configurations were equally likely, we would have  $(\Delta S)_{\text{riffle}} = \log_2 \binom{52}{26} = 48.817$ . However, they are not all equally likely. For example, the probability that we drop the entire left-half deck and then the entire right half-deck is  $2^{-26}$ . After the last card from the left half-deck is dropped, we have no more choices to make. On the other hand, the probability for the sequence LRLR... is  $2^{-51}$ , because it is only after the 51<sup>st</sup> card is dropped that we have no more choices. We can derive an exact expression for the entropy of the riffle shuffle in the following manner. Consider a deck of  $N = 2K$  cards. The probability that we run out of choices after  $K$  cards is the probability of the first  $K$  cards dropped being all from one particular half-deck, which is  $2 \cdot 2^{-K}$ . Now let's ask what is the probability that we run out of choices after  $(K + 1)$  cards are dropped. If all the remaining  $(K - 1)$  cards are from the right half-deck, this means that we must have one of the R cards among the first  $K$  dropped. Note that this R card cannot be the  $(K + 1)$ <sup>th</sup> card dropped, since then all of the first  $K$  cards are L, which we have already considered. Thus, there are  $\binom{K}{1} = K$  such configurations, each with a probability  $2^{-K-1}$ . Next, suppose we run out of choices after  $(K + 2)$  cards are dropped. If the remaining  $(K - 2)$  cards are R, this means we must have 2 of the R cards among the first  $(K + 1)$  dropped, which means  $\binom{K+1}{2}$  possibilities. Note that the  $(K + 2)$ <sup>th</sup> card must be L, since if it were R this would mean that the last  $(K - 1)$  cards are R, which we have already considered. Continuing in this manner, we conclude

$$\Omega_K = 2 \sum_{n=0}^K \binom{K+n-1}{n} = \binom{2K}{K}$$

and

$$S_K = - \sum_{a=1}^{\Omega_K} p_a \log_2 p_a = \sum_{n=0}^{K-1} \binom{K+n-1}{n} \cdot 2^{-(K+n)} \cdot (K+n).$$

The results are tabulated below in Table 1. For a deck of 52 cards, the actual entropy per riffle shuffle is  $S_{26} = 46.274$ .

(d) Ignoring redundancies, we require  $k = S_{\text{random}}/(\Delta S)_{\text{riffle}} = 4.62$  shuffles if we assume all riffle outcomes are equally likely, and 4.88 if we use the exact result for the riffle entropy. Since there are no fractional shuffles, we round up to  $k = 5$  in both cases. In fact, computer experiments show that the answer is  $k = 9$ . The reason we are so far off is that we have ignored redundancies, *i.e.* we have assumed that all the states produced by two consecutive riffle shuffles are distinct. They are not! For decks with asymptotically large

$K$	$\Omega_K$	$S_K$	$\log_2 \binom{2K}{K}$
2	6	2.500	2.585
12	2704156	20.132	20.367
26	$4.96 \times 10^{14}$	46.274	48.817
100	$9.05 \times 10^{58}$	188.730	195.851

Table 1: Riffle shuffle results.

numbers of cards  $N \gg 1$ , the number of riffle shuffles required is  $k \simeq \frac{3}{2} \log_2 N$ . See D. Bayer and P. Diaconis, *Annals of Applied Probability* 2, 294 (1992).

(e) Using the first four terms of Stirling's approximation of  $\ln K$ , i.e. out to  $\mathcal{O}(K^0)$ , we find  $\log_2 52! \approx 225.579$  and  $\log_2 \binom{52}{26} \approx 48.824$ .

(2) In problem #1, we ran across Stirling's approximation,

$$\ln K! \sim K \ln K - K + \frac{1}{2} \ln(2\pi K) + \mathcal{O}(K^{-1}),$$

for large  $K$ . In this exercise, you will derive this expansion.

(a) Start by writing

$$K! = \int_0^\infty dx x^K e^{-x},$$

and define  $x \equiv K(t+1)$  so that  $K! = K^{K+1} e^{-K} F(K)$ , where

$$F(K) = \int_{-1}^\infty dt e^{Kf(t)}.$$

Find the function  $f(t)$ .

- (b) Expand  $f(t) = \sum_{n=0}^\infty f_n t^n$  in a Taylor series and find a general formula for the expansion coefficients  $f_n$ . In particular, show that  $f_0 = f_1 = 0$  and that  $f_2 = -\frac{1}{2}$ .
- (c) If one ignores all the terms but the lowest order (quadratic) in the expansion of  $f(t)$ , show that

$$\int_{-1}^\infty dt e^{-Kt^2/2} = \sqrt{\frac{2\pi}{K}} - R(K),$$

and show that the remainder  $R(K) > 0$  is bounded from above by a function which decreases faster than any polynomial in  $1/K$ .

(d) *For the brave only!* – Find the  $\mathcal{O}(K^{-1})$  term in the expansion for  $\ln K!$ .

**Solution :**

(a) Setting  $x = K(t + 1)$ , we have

$$K! = K^{K+1} e^{-K} \int_{-1}^{\infty} dt (t + 1)^K e^{-t},$$

hence  $f(t) = \ln(t + 1) - t$ .

(b) The Taylor expansion of  $f(t)$  is

$$f(t) = -\frac{1}{2}t^2 + \frac{1}{3}t^3 - \frac{1}{4}t^4 + \dots$$

(c) Retaining only the leading term in the Taylor expansion of  $f(t)$ , we have

$$\begin{aligned} F(K) &\simeq \int_{-1}^{\infty} dt e^{-Kt^2/2} \\ &= \sqrt{\frac{2\pi}{K}} - \int_1^{\infty} dt e^{-Kt^2/2}. \end{aligned}$$

Writing  $t \equiv s + 1$ , the remainder is found to be

$$R(K) = e^{-K/2} \int_0^{\infty} ds e^{-Ks^2/2} e^{-Ks} < \sqrt{\frac{\pi}{2K}} e^{-K/2},$$

which decreases exponentially with  $K$ , faster than any power.

(d) We have

$$\begin{aligned} F(K) &= \int_{-1}^{\infty} dt e^{-\frac{1}{2}Kt^2} e^{\frac{1}{3}Kt^3 - \frac{1}{4}Kt^4 + \dots} \\ &= \int_{-1}^{\infty} dt e^{-\frac{1}{2}Kt^2} \left\{ 1 + \frac{1}{3}Kt^3 - \frac{1}{4}Kt^4 + \frac{1}{18}K^2t^6 + \dots \right\} \\ &= \sqrt{\frac{2\pi}{K}} \cdot \left\{ 1 - \frac{3}{4}K^{-1} + \frac{5}{6}K^{-1} + \mathcal{O}(K^{-2}) \right\} \end{aligned}$$

Thus,

$$\ln K! = K \ln K - K + \frac{1}{2} \ln K + \frac{1}{2} \ln(2\pi) + \frac{1}{12} K^{-1} + \mathcal{O}(K^{-2}).$$

(3) A six-sided die is loaded so that the probability to throw a three is twice that of throwing a two, and the probability of throwing a four is twice that of throwing a five.

- (a) Find the distribution  $\{p_n\}$  consistent with maximum entropy, given these constraints.  
 (b) Assuming the maximum entropy distribution, given two such identical dice, what is the probability to roll a total of seven if both are thrown simultaneously?

**Solution :**

(a) We have the following constraints:

$$\begin{aligned} X^0(\mathbf{p}) &= p_1 + p_2 + p_3 + p_4 + p_5 + p_6 - 1 = 0 \\ X^1(\mathbf{p}) &= p_3 - 2p_2 = 0 \\ X^2(\mathbf{p}) &= p_4 - 2p_5 = 0 . \end{aligned}$$

We define

$$S^*(\mathbf{p}, \boldsymbol{\lambda}) \equiv - \sum_n p_n \ln p_n - \sum_{a=0}^2 \lambda_a X^{(a)}(\mathbf{p}) ,$$

and freely extremize over the probabilities  $\{p_1, \dots, p_6\}$  and the undetermined Lagrange multipliers  $\{\lambda_0, \lambda_1, \lambda_2\}$ . We obtain

$$\begin{aligned} \frac{\partial S^*}{\partial p_1} &= -1 - \ln p_1 - \lambda_0 & \frac{\partial S^*}{\partial p_4} &= -1 - \ln p_4 - \lambda_0 - \lambda_2 \\ \frac{\partial S^*}{\partial p_2} &= -1 - \ln p_2 - \lambda_0 + 2\lambda_1 & \frac{\partial S^*}{\partial p_5} &= -1 - \ln p_5 - \lambda_0 + 2\lambda_2 \\ \frac{\partial S^*}{\partial p_3} &= -1 - \ln p_3 - \lambda_0 - \lambda_1 & \frac{\partial S^*}{\partial p_6} &= -1 - \ln p_6 - \lambda_0 . \end{aligned}$$

Extremizing with respect to the undetermined multipliers generates the three constraint equations. We therefore have

$$\begin{aligned} p_1 &= e^{-\lambda_0 - 1} & p_4 &= e^{-\lambda_0 - 1} e^{-\lambda_2} \\ p_2 &= e^{-\lambda_0 - 1} e^{2\lambda_1} & p_5 &= e^{-\lambda_0 - 1} e^{2\lambda_2} \\ p_3 &= e^{-\lambda_0 - 1} e^{-\lambda_1} & p_6 &= e^{-\lambda_0 - 1} . \end{aligned}$$

We solve for  $\{\lambda_0, \lambda_1, \lambda_2\}$  by imposing the three constraints. Let  $x \equiv p_1 = p_6 = e^{-\lambda_0 - 1}$ . Then  $p_2 = x e^{2\lambda_1}$ ,  $p_3 = x e^{-\lambda_1}$ ,  $p_4 = x e^{-\lambda_2}$ , and  $p_5 = x e^{2\lambda_2}$ . We then have

$$\begin{aligned} p_3 = 2p_2 &\Rightarrow e^{-3\lambda_1} = 2 \\ p_4 = 2p_5 &\Rightarrow e^{-3\lambda_2} = 2 . \end{aligned}$$

We may now solve for  $x$ :

$$\sum_{n=1}^6 p_n = (2 + 2^{1/3} + 2^{4/3}) x = 1 \quad \Rightarrow \quad x = \frac{1}{2 + 3 \cdot 2^{1/3}} .$$

We now have all the probabilities:

$$\begin{aligned} p_1 = x &= 0.1730 & p_4 &= 2^{1/3} x = 0.2180 \\ p_2 &= 2^{-2/3} x = 0.1090 & p_5 &= 2^{-2/3} x = 0.1090 \\ p_3 &= 2^{1/3} x = 0.2180 & p_6 &= x = 0.1730 . \end{aligned}$$

(b) The probability to roll a seven with two of these dice is

$$\begin{aligned} P(7) &= 2 p_1 p_6 + 2 p_2 p_5 + 2 p_3 p_4 \\ &= 2 (1 + 2^{-4/3} + 2^{2/3}) x^2 = 0.1787 . \end{aligned}$$

(4) The probability density for a random variable  $x$  is given by the Lorentzian,

$$P(x) = \frac{\gamma}{\pi} \cdot \frac{1}{x^2 + \gamma^2} .$$

Consider the sum  $X_N = \sum_{i=1}^N x_i$ , where each  $x_i$  is independently distributed according to  $P(x_i)$ . Find the probability  $P_N(Y)$  that  $|X_N| < Y$ , where  $Y > 0$  is arbitrary.

**Solution :**

As discussed in the Lecture Notes §1.4.2, the distribution of a sum of identically distributed random variables,  $X = \sum_{i=1}^N x_i$ , is given by

$$P_N(X) = \int_{-\infty}^{\infty} \frac{dk}{2\pi} [\hat{P}(k)]^N e^{ikX} ,$$

where  $\hat{P}(k)$  is the Fourier transform of the probability distribution  $P(x_i)$  for each of the  $x_i$ . The Fourier transform of a Lorentzian is an exponential:

$$\int_{-\infty}^{\infty} dx P(x) e^{-ikx} = e^{-\gamma|k|} .$$

Thus,

$$\begin{aligned} P_N(X) &= \int_{-\infty}^{\infty} \frac{dk}{2\pi} e^{-N\gamma|k|} e^{ikX} \\ &= \frac{N\gamma}{\pi} \cdot \frac{1}{X^2 + N^2\gamma^2} . \end{aligned}$$

The probability for  $X$  to lie in the interval  $X \in [-Y, Y]$ , where  $Y > 0$ , is

$$H_N(Y) = \int_{-Y}^Y dX P_N(X) = \frac{2}{\pi} \tan^{-1} \left( \frac{Y}{N\gamma} \right).$$

The integral is easily performed with the substitution  $X = N\gamma \tan \theta$ . Note that  $H_N(0) = 0$  and  $H_N(\infty) = 1$ .

**PHYSICS 140A : STATISTICAL PHYSICS**  
**HW ASSIGNMENT #2 SOLUTIONS**

(1) A box of volume  $V$  contains  $N_1$  identical atoms of mass  $m_1$  and  $N_2$  identical atoms of mass  $m_2$ .

- (a) Compute the density of states  $D(E, V, N_1, N_2)$ .
- (b) Let  $x_1 \equiv N_1/N$  be the fraction of particles of species #1. Compute the statistical entropy  $S(E, V, N, x_1)$ .
- (c) Under what conditions does increasing the fraction  $x_1$  result in an increase in statistical entropy of the system? Why?

**Solution :**

(a) Following the method outlined in §4.2.2 of the Lecture Notes, we rescale all the momenta  $p_i$  with  $i \in \{1, \dots, N_1\}$  as  $p_i^\alpha = \sqrt{2m_1 E} u_i^\alpha$ , and all the momenta  $p_j$  with  $j \in \{N_1 + 1, \dots, N_1 + N_2\}$  as  $p_j^\alpha = \sqrt{2m_2 E} u_j^\alpha$ . We then have

$$D(E, V, N_1, N_2) = \frac{V^{N_1+N_2}}{N_1! N_2!} \left( \frac{\sqrt{2m_1 E}}{h} \right)^{N_1 d} \left( \frac{\sqrt{2m_2 E}}{h} \right)^{N_2 d} E^{-1} \cdot \frac{1}{2} \Omega_{(N_1+N_2)d}.$$

Thus,

$$D(E, V, N_1, N_2) = \frac{V^N}{N_1! N_2!} \left( \frac{m}{2\pi\hbar^2} \right)^{\frac{1}{2}Nd} \frac{E^{\frac{1}{2}Nd-1}}{\Gamma(Nd/2)},$$

where  $N = N_1 + N_2$  and  $m \equiv m_1^{N_1/N} m_2^{N_2/N}$  has dimensions of mass. Note that the  $N_1! N_2!$  term in the denominator, in contrast to  $N!$ , appears because only particles of the same species are identical.

(b) Using Stirling's approximation  $\ln K! \simeq K \ln K - K + \mathcal{O}(\ln K)$ , we find

$$\frac{S}{k_B} = \ln D = N \ln \left( \frac{V}{N} \right) + \frac{1}{2} Nd \ln \left( \frac{2E}{Nd} \right) - N(x_1 \ln x_1 + x_2 \ln x_2) + \frac{1}{2} Nd \ln \left( \frac{m_1^{x_1} m_2^{x_2}}{2\pi\hbar^2} \right) + N(1 + \frac{1}{2}d),$$

where  $x_2 = 1 - x_1$ .

(c) Using  $x_2 = 1 - x_1$ , we have

$$\frac{\partial S}{\partial x_1} = N \ln \left( \frac{1 - x_1}{x_1} \right) + \frac{1}{2} Nd \ln \left( \frac{m_1}{m_2} \right).$$

Setting  $\partial S / \partial x_1$  to zero at the solution  $x = x_1^*$ , we obtain

$$x_1^* = \frac{m_1^{d/2}}{m_1^{d/2} + m_2^{d/2}}, \quad x_2^* = \frac{m_2^{d/2}}{m_1^{d/2} + m_2^{d/2}}.$$

Thus, an increase of  $x_1$  will result in an increase in statistical entropy if  $x_1 < x_1^*$ . The reason is that  $x_1 = x_1^*$  is optimal in terms of maximizing  $S$ .



**(2)** Two chambers containing Argon gas at  $p = 1.0 \text{ atm}$  and  $T = 300 \text{ K}$  are connected via a narrow tube. One chamber has volume  $V_1 = 1.0 \text{ L}$  and the other has volume  $V_2 = r V_1$ .

- Compute the RMS energy fluctuations of the particles in the smaller chamber when the volume ratio is  $r = 2$ .
- Compute the RMS energy fluctuations of the particles in the smaller chamber when the volume ratio is  $r = \infty$ .

**Solution :**

For two systems in thermal contact (see Lecture Notes §4.5), the RMS energy fluctuation of system #1 is  $\Delta E_1 = \sqrt{k_B T^2 \bar{C}_V}$ , where

$$\bar{C}_V = \frac{C_{V,1} C_{V,2}}{C_{V,1} + C_{V,2}} = \frac{r}{r+1} C_{V,1}.$$

Thus, with  $C_V = \frac{3}{2} N k_B = 3pV/T$ , we have

$$\Delta E_1 = \sqrt{\frac{r}{r+1}} \cdot \sqrt{\frac{3}{2} pV k_B T} = \sqrt{\frac{r}{r+1}} \cdot 7.93 \times 10^{-10} \text{ J}.$$

Thus, (a) for  $r = 2$  we have  $\Delta E_1 = 648 \text{ pJ}$ , and (b) for  $r = \infty$  we have  $\Delta E_1 = 793 \text{ pJ}$ , where  $1 \text{ pJ} = 10^{-12} \text{ J}$ .

**(3)** Consider a system of  $N$  identical but distinguishable particles, each of which has a nondegenerate ground state with energy zero, and a  $g$ -fold degenerate excited state with energy  $\varepsilon > 0$ .

- Let the total energy of the system be fixed at  $E = M\varepsilon$ , where  $M$  is the number of particles in an excited state. What is the total number of states  $\Omega(E, N)$ ?
- What is the entropy  $S(E, N)$ ? Assume the system is thermodynamically large. You may find it convenient to define  $\nu \equiv M/N$ , which is the fraction of particles in an excited state.
- Find the temperature  $T(\nu)$ . Invert this relation to find  $\nu(T)$ .
- Show that there is a region where the temperature is negative.
- What happens when a system at negative temperature is placed in thermal contact with a heat bath at positive temperature?

**Solution :**

(a) Since each excited particle can be in any of  $g$  degenerate energy states, we have

$$\Omega(E, N) = \binom{N}{M} g^M = \frac{N! g^M}{M! (N - M)!}.$$

(b) Using Stirling's approximation, we have

$$S(E, N) = k_B \ln \Omega(E, N) = -Nk_B \left\{ \nu \ln \nu + (1 - \nu) \ln(1 - \nu) - \nu \ln g \right\},$$

where  $\nu = M/N = E/N\varepsilon$ .

(c) The inverse temperature is

$$\frac{1}{T} = \left( \frac{\partial S}{\partial E} \right)_N = \frac{1}{N\varepsilon} \left( \frac{\partial S}{\partial \nu} \right)_N = \frac{k_B}{\varepsilon} \cdot \left\{ \ln \left( \frac{1 - \nu}{\nu} \right) + \ln g \right\},$$

hence

$$k_B T = \frac{\varepsilon}{\ln \left( \frac{1 - \nu}{\nu} \right) + \ln g}.$$

Inverting,

$$\nu(T) = \frac{g e^{-\varepsilon/k_B T}}{1 + g e^{-\varepsilon/k_B T}}.$$

(d) The temperature diverges when the denominator in the above expression for  $T(\nu)$  vanishes. This occurs at  $\nu = \nu^* \equiv g/(g + 1)$ . For  $\nu \in (\nu^*, 1)$ , the temperature is negative! This is technically correct, and a consequence of the fact that the energy is bounded for this system:  $E \in [0, N\varepsilon]$ . The entropy as a function of  $\nu$  therefore has a maximum at  $\nu = \nu^*$ . The model is unphysical though in that it neglects various excitations such as kinetic energy (e.g. lattice vibrations) for which the energy can be arbitrarily large.

(e) When a system at negative temperature is placed in contact with a heat bath at positive temperature, heat flows from the system to the bath. The energy of the system therefore decreases, and since  $\frac{\partial S}{\partial E} < 0$ , this results in a net entropy increase, which is what is demanded by the Second Law of Thermodynamics.

**(4)** Solve for the model in problem 3 using the ordinary canonical ensemble. The Hamiltonian is

$$\hat{H} = \varepsilon \sum_{i=1}^N (1 - \delta_{\sigma_i, 1}),$$

where  $\sigma_i \in \{1, \dots, g + 1\}$ .

(a) Find the partition function  $Z(T, N)$  and the Helmholtz free energy  $F(T, N)$ .

- (b) Show that  $\hat{M} = \frac{\partial \hat{H}}{\partial \varepsilon}$  counts the number of particles in an excited state. Evaluate the thermodynamic average  $\nu(T) = \langle \hat{M} \rangle / N$ .
- (c) Show that the entropy  $S = - \left( \frac{\partial F}{\partial T} \right)_N$  agrees with your result from problem 3.

**Solution :**

(a) We have

$$Z(T, N) = \text{Tr} e^{-\beta \hat{H}} = (1 + g e^{-\varepsilon/k_B T})^N .$$

The free energy is

$$F(T, N) = -k_B T \ln Z(T, N) = -N k_B T \ln (1 + g e^{-\varepsilon/k_B T}) .$$

(b) We have

$$\hat{M} = \frac{\partial \hat{H}}{\partial \varepsilon} = \sum_{i=1}^N (1 - \delta_{\sigma_i, 1}) .$$

Clearly this counts all the excited particles, since the expression  $1 - \delta_{\sigma_i, 1}$  vanishes if  $i = 1$ , which is the ground state, and yields 1 if  $i \neq 1$ , i.e. if particle  $i$  is in any of the  $g$  excited states. The thermodynamic average of  $\hat{M}$  is  $\langle \hat{M} \rangle = \left( \frac{\partial F}{\partial \varepsilon} \right)_{T, N}$ , hence

$$\nu = \frac{\langle \hat{M} \rangle}{N} = \frac{g e^{-\varepsilon/k_B T}}{1 + g e^{-\varepsilon/k_B T}} ,$$

which agrees with the result in problem 3c.

(c) The entropy is

$$S = - \left( \frac{\partial F}{\partial T} \right)_N = N k_B \ln(1 + g e^{-\varepsilon/k_B T}) + \frac{N \varepsilon}{T} \frac{g e^{-\varepsilon/k_B T}}{1 + g e^{-\varepsilon/k_B T}} .$$

Working with our result for  $\nu(T)$ , we derive

$$1 + g e^{-\varepsilon/k_B T} = \frac{1}{1 - \nu}$$

$$\frac{\varepsilon}{k_B T} = \ln \left( \frac{g(1 - \nu)}{\nu} \right) .$$

Inserting these results into the above expression for  $S$ , we verify

$$S = -N k_B \ln(1 - \nu) + N k_B \nu \ln \left( \frac{g(1 - \nu)}{\nu} \right)$$

$$= -N k_B \left\{ \nu \ln \nu + (1 - \nu) \ln(1 - \nu) - \nu \ln g \right\} ,$$

as we found in problem 3b.

**PHYSICS 140A : STATISTICAL PHYSICS**  
**HW ASSIGNMENT #3 SOLUTIONS**

(1) Consider a system described by the Hamiltonian

$$\hat{H} = -H \sum_{i=1}^N \sigma_i + \Delta \sum_{i=1}^N (1 - \sigma_i^2),$$

where each  $\sigma_i \in \{-1, 0, +1\}$ .

- (a) Compute the ordinary canonical partition function  $Z(T, N, H, \Delta)$  and the free energy  $F(T, N, H, \Delta)$ .
- (b) Find the magnetization  $M(T, N, H, \Delta)$ .
- (c) Show that  $\frac{\partial M}{\partial \Delta} = -\frac{\partial N_0}{\partial H}$ , where  $N_0 = \sum_{i=1}^N \delta_{\sigma_i, 0}$ .

**Solution :**

(a) We have

$$Z(T, V, N, \Delta) = \left( e^{\beta H} + e^{-\beta \Delta} + e^{-\beta H} \right)^N$$

$$F(T, V, N, \Delta) = -N k_B T \ln \left( 2 \cosh(\beta H) + e^{-\beta \Delta} \right)$$

(b) The thermodynamic magnetization is given by

$$M = - \left( \frac{\partial F}{\partial H} \right)_{N, \Delta} = \frac{N \sinh(\beta H)}{\cosh(\beta H) + \frac{1}{2} e^{-\beta \Delta}}.$$

(c) The Hamiltonian can be written  $\hat{H} = -HM + \Delta N_0$ , since  $\delta_{\sigma, 0} = 1 - \sigma^2$  when  $\sigma \in \{-1, 0, +1\}$ . Thus,

$$N_0 = + \left( \frac{\partial F}{\partial \Delta} \right)_{H, N} \Rightarrow -\frac{\partial^2 F}{\partial H \partial \Delta} = \frac{\partial M}{\partial \Delta} = -\frac{\partial N_0}{\partial H}.$$

(2) Consider a three-dimensional gas of  $N$  identical particles of mass  $m$ , each of which has a magnetic dipole moment  $\mathbf{m} = \mu_0 \hat{\mathbf{n}}$ , where  $\hat{\mathbf{n}}$  is a three-dimensional unit vector. The Hamiltonian is

$$\hat{H} = \sum_{i=1}^N \left[ \frac{\mathbf{p}_i^2}{2m} - \mu_0 \mathbf{H} \cdot \hat{\mathbf{n}}_i \right].$$

- (a) What is the grand potential  $\Omega(T, V, \mu, \mathbf{H})$ ?
- (b) Express  $\mathbf{M}$  in terms of  $T, V, N$ , and  $\mathbf{H}$ , where  $N$  is the average number of particles.
- (c) Find  $M(T, V, N, \mathbf{H})$  to lowest order in the external field.

**Solution :**

(a) The contribution from the orientational ( $\hat{\mathbf{n}}$ ) degrees of freedom to the single particle partition function is

$$\xi_{\hat{\mathbf{n}}} = \int \frac{d\hat{\mathbf{n}}}{4\pi} e^{\beta\mu_0\mathbf{H}\cdot\hat{\mathbf{n}}} = \frac{1}{2} \int_{-1}^1 dx e^{\beta\mu_0 Hx} = \frac{\sinh(\beta\mu_0 H)}{\beta\mu_0 H},$$

where the integral is done by choosing the  $\hat{z}$ -axis to lie along  $\mathbf{H}$ , then integrating out over the azimuthal angle  $\phi$  (yielding  $2\pi$ ), and finally over  $x = \hat{\mathbf{H}} \cdot \hat{\mathbf{n}} = \cos\theta$ . Then

$$\xi(T, H) = V\lambda_T^{-d} \xi_{\hat{\mathbf{n}}}(T, H)$$

and so  $Z(T, V, \mu, \mathbf{H}) = \xi^N/N!$  is the canonical partition function. The grand potential, following the discussion in the Lecture Notes, is then

$$\Omega(T, V, \mu, \mathbf{H}) = -Vk_B T \lambda_T^{-d} e^{\mu/k_B T} \cdot \frac{\sinh(\mu_0 H/k_B T)}{\mu_0 H/k_B T}.$$

(b) Let  $\alpha \equiv \mu_0 H/k_B T$ , and define  $\xi(\alpha) = \alpha^{-1} \sinh \alpha$ . We have

$$\mathbf{M} = -\frac{\partial \Omega}{\partial \mathbf{H}} = V\lambda_T^{-d} e^{\mu/k_B T} \cdot \mu_0 \hat{\mathbf{H}} \xi'(\alpha) \Big|_{\alpha=\mu_0 H/k_B T}.$$

The particle number is

$$N = -\frac{\partial \Omega}{\partial \mu} = V\lambda_T^{-d} e^{\mu/k_B T} \xi(\alpha),$$

hence

$$\mathbf{M} = N\mu_0 \hat{\mathbf{H}} \cdot \frac{\xi'(\alpha)}{\xi(\alpha)} = N\mu_0 \hat{\mathbf{H}} \cdot \left( \operatorname{ctnh} \alpha - \alpha^{-1} \right).$$

Note that we have here used

$$\frac{\partial H}{\partial \mathbf{H}} = \hat{\mathbf{H}} = \frac{\mathbf{H}}{H},$$

where  $H = |\mathbf{H}|$ .

(c) We expand  $\operatorname{ctnh} \alpha = \frac{1}{\alpha} + \frac{\alpha}{3} + \mathcal{O}(\alpha^3)$  in a Laurent series. To lowest order in  $\mathbf{H}$ , then,

$$\mathbf{M} = \frac{N\mu_0^2 \mathbf{H}}{3k_B T}.$$

**PHYSICS 140A : STATISTICAL PHYSICS**  
**HW ASSIGNMENT #4 SOLUTIONS**

(1) Consider a  $d$ -dimensional ultrarelativistic gas of classical indistinguishable particles with a dispersion  $\varepsilon(\mathbf{p}) = c|\mathbf{p}|$ .

- (a) Find an expression for the grand potential  $\Omega(T, V, \mu)$ .
- (b) Find the average number of particles  $N(T, V, \mu)$ .
- (c) Find the entropy  $S(T, V, \mu)$ .
- (d) Express the RMS fluctuations in the number of particle number,  $(\Delta N)_{\text{RMS}}$ , in terms of the volume  $V$ , temperature  $T$ , and the pressure  $p$ .

**Solution :**

(a) The OCE partition function  $Z(T, V, N)$  is computed in §4.2.4 of the Lecture Notes. One finds

$$Z(T, V, N) = \frac{V^N}{N!} \left( \frac{\Gamma(d) \Omega_d}{(\beta hc)^d} \right)^N .$$

From  $\Xi = e^{-\beta\Omega} = \sum_{N=0}^{\infty} e^{\beta\mu N} Z(T, V, N)$ , we obtain

$$\Omega(T, V, \mu) = -\frac{\Gamma(d)\Omega_d}{(hc)^d} V (k_B T)^{d+1} e^{\mu/k_B T} .$$

(b) The particle number is

$$N(T, V, \mu) = -\left( \frac{\partial \Omega}{\partial \mu} \right)_{T, V} = -(d+1) \frac{\Gamma(d)\Omega_d}{(hc)^d} V (k_B T)^d e^{\mu/k_B T}$$

(c) The entropy is

$$S(T, V, \mu) = -\left( \frac{\partial \Omega}{\partial T} \right)_{V, \mu} = \left( (d+1)k_B - \frac{\mu}{T} \right) \frac{\Gamma(d)\Omega_d}{(hc)^d} V (k_B T)^d e^{\mu/k_B T} .$$

(d) The variance of the number  $\hat{N}$  is (see eqn. 4.138 of the Lecture Notes)

$$\text{var}(\hat{N}) = k_B T \left( \frac{\partial N}{\partial \mu} \right)_{T, V} = N = \frac{pV}{k_B T} .$$

Thus,

$$(\Delta N)_{\text{RMS}} = \sqrt{\text{var}(\hat{N})} = \left( \frac{pV}{k_B T} \right)^{1/2} .$$

(2) Consider again the  $d$ -dimensional classical ultrarelativistic gas with  $\varepsilon(\mathbf{p}) = cp$ .

- (a) If  $d = 3$ , find the momentum distribution function  $g(\mathbf{p})$ .
- (b) Again for  $d = 3$ , find a general formula for the moments  $\langle |\mathbf{p}|^k \rangle$ .
- (c) Repeat parts (a) and (b) for the case  $d = 2$ .
- (d) In  $d = 3$ , what is the distribution function  $f(\mathbf{v})$  for velocities?

**Solution :**

(a) We have

$$g(\mathbf{p}) = \langle \delta(\mathbf{p} - \mathbf{p}_1) \rangle = \frac{e^{-\beta cp}}{\int d^3p e^{-\beta cp}} = \frac{c^3}{8\pi(k_B T)^3} e^{-\beta cp}.$$

(b) The moments are

$$\langle |\mathbf{p}|^k \rangle = \frac{1}{2}(\beta c)^3 \int_0^\infty dp p^{2+k} e^{-\beta cp} = \frac{1}{2}(k+2)! (\beta c)^{-k}$$

(c) In  $d = 2$ ,

$$g(\mathbf{p}) = \langle \delta(\mathbf{p} - \mathbf{p}_1) \rangle = \frac{e^{-\beta cp}}{\int d^2p e^{-\beta cp}} = \frac{c^2}{2\pi(k_B T)^2} e^{-\beta cp}$$

and

$$\langle |\mathbf{p}|^k \rangle = (\beta c)^2 \int_0^\infty dp p^{1+k} e^{-\beta cp} = (k+1)! (\beta c)^{-k}$$

(d) The velocity is  $\mathbf{v} = \frac{\partial \varepsilon}{\partial \mathbf{p}} = c \hat{\mathbf{p}}$ . Thus, the magnitude is fixed at  $|\mathbf{v}| = c$  and the direction is distributed isotropically, *i.e.*

$$f(\mathbf{v}) = \frac{\delta(v - c)}{4\pi c^2}.$$

(3) A classical gas of indistinguishable particles in three dimensions is described by the Hamiltonian

$$\hat{H} = \sum_{i=1}^N \left\{ A |\mathbf{p}_i|^3 - \mu_0 H S_i \right\},$$

where  $A$  is a constant, and where  $S_i \in \{-1, 0, +1\}$  (*i.e.* there are three possible spin polarization states).

- (a) Compute the free energy  $F_{\text{gas}}(T, H, V, N)$ .
- (b) Compute the magnetization density  $m_{\text{gas}} = M_{\text{gas}}/V$  as a function of temperature, pressure, and magnetic field.

The gas is placed in thermal contact with a surface containing  $N_s$  adsorption sites, each with adsorption energy  $-\Delta$ . The surface is metallic and shields the adsorbed particles from the magnetic field, so the field at the surface may be approximated by  $H = 0$ .

- (c) Find the Landau free energy for the surface,  $\Omega_{\text{surf}}(T, N_s, \mu)$ .
- (d) Find the fraction  $f_0(T, \mu)$  of empty adsorption sites.
- (e) Find the gas pressure  $p^*(T, H)$  at which  $f_0 = \frac{1}{2}$ .

**Solution :**

(a) The single particle partition function is

$$\zeta(T, V, H) = V \int \frac{d^3p}{h^3} e^{-Ap^3/k_B T} \sum_{S=-1}^1 e^{\mu_0 HS/k_B T} = \frac{4\pi V k_B T}{3Ah^3} \cdot \left(1 + 2 \cosh(\mu_0 H/k_B T)\right).$$

The  $N$ -particle partition function is  $Z_{\text{gas}}(T, H, V, N) = \zeta^N/N!$ , hence

$$F_{\text{gas}} = -Nk_B T \left[ \ln \left( \frac{4\pi V k_B T}{3NAh^3} \right) + 1 \right] - Nk_B T \ln \left( 1 + 2 \cosh(\mu_0 H/k_B T) \right)$$

(b) The magnetization density is

$$m_{\text{gas}}(T, p, H) = -\frac{1}{V} \frac{\partial F}{\partial H} = \frac{p\mu_0}{k_B T} \cdot \frac{2 \sinh(\mu_0 H/k_B T)}{1 + 2 \cosh(\mu_0 H/k_B T)}$$

We have used the ideal gas law,  $pV = Nk_B T$  here.

(c) There are four possible states for an adsorption site: empty, or occupied by a particle with one of three possible spin polarizations. Thus,  $\Xi_{\text{surf}}(T, N_s, \mu) = \xi^{N_s}$ , with

$$\xi(T, \mu) = 1 + 3 e^{(\mu+\Delta)/k_B T}.$$

Thus,

$$\Omega_{\text{surf}}(T, N_s, \mu) = -N_s k_B T \ln \left( 1 + 3 e^{(\mu+\Delta)/k_B T} \right)$$

(d) The fraction of empty adsorption sites is  $1/\xi$ , i.e.

$$f_0(T, \mu) = \frac{1}{1 + 3 e^{(\mu+\Delta)/k_B T}}$$



(e) Setting  $f_0 = \frac{1}{2}$ , we obtain the equation  $3 e^{(\mu+\Delta)/k_B T} = 1$ , or

$$e^{\mu/k_B T} = \frac{1}{3} e^{-\Delta/k_B T} .$$

We now need the fugacity  $z = e^{\mu/k_B T}$  in terms of  $p$ ,  $T$ , and  $H$ . To this end, we compute the Landau free energy of the gas,

$$\Omega_{\text{gas}} = -pV = -k_B T \zeta e^{\mu/k_B T} .$$

Thus,

$$p^*(T, H) = \frac{k_B T \zeta}{V} e^{\mu/k_B T} = \frac{4\pi(k_B T)^2}{9Ah^3} \cdot \left(1 + 2 \cosh(\mu_0 H/k_B T)\right) e^{-\Delta/k_B T}$$

**PHYSICS 140A : STATISTICAL PHYSICS**  
**HW ASSIGNMENT #5 SOLUTIONS**

(1) Consider a system composed of  $N$  spin tetramers, each of which is described by a Hamiltonian

$$\hat{H} = -J(\sigma_1\sigma_2 + \sigma_1\sigma_3 + \sigma_1\sigma_4 + \sigma_2\sigma_3 + \sigma_2\sigma_4 + \sigma_3\sigma_4) - K\sigma_1\sigma_2\sigma_3\sigma_4 - \mu_0 H(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4).$$

The individual tetramers are otherwise noninteracting.

- (a) Find the single tetramer partition function  $\zeta$ . *Suggestion: construct a table of all the possible tetramer states and their energies.*
- (b) Find the magnetization per tetramer  $m = \mu_0 \langle \sigma_1 + \sigma_2 + \sigma_3 + \sigma_4 \rangle$ .
- (c) Suppose the tetramer number density is  $n_t$ . The magnetization density is  $M = n_t m$ . Find the zero field susceptibility  $\chi(T) = (\partial M / \partial H)_{H=0}$ .

**Solution :**

(a) First, note that

$$-J(\sigma_1\sigma_2 + \sigma_1\sigma_3 + \sigma_1\sigma_4 + \sigma_2\sigma_3 + \sigma_2\sigma_4 + \sigma_3\sigma_4) = 2J - \frac{1}{2}J(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4)^2.$$

Next, construct a table, as in Tab. 1. We see that

$$\zeta = 2e^{\beta(6J+K)} \cosh(4\beta\mu_0 H) + 8e^{-\beta K} \cosh(2\beta\mu_0 H) + 6e^{-\beta(2J-K)}.$$

(b) We have

$$m = \frac{1}{\beta \zeta} \cdot \frac{\partial \zeta}{\partial H} = \frac{4\mu_0 e^{\beta(6J+K)} \sinh(4\beta\mu_0 H) + 8\mu_0 e^{-\beta K} \sinh(2\beta\mu_0 H)}{e^{\beta(6J+K)} \cosh(4\beta\mu_0 H) + 4e^{-\beta K} \cosh(2\beta\mu_0 H) + 3e^{-\beta(2J-K)}}$$

(c) In the limit  $H \rightarrow 0$ , we have

$$M(T, H) = n_t m(T, H) = \frac{16\beta\mu_0^2 e^{\beta(6J+K)} + 16\beta\mu_0^2 e^{-\beta K}}{e^{\beta(6J+K)} + 4e^{-\beta K} + 3e^{-\beta(2J-K)}} \cdot n_t,$$

so

$$\chi(T) = \frac{16n_t\mu_0^2}{k_B T} \cdot \frac{e^{(6J+K)/k_B T} + e^{-K/k_B T}}{e^{(6J+K)/k_B T} + 4e^{-K/k_B T} + 3e^{-(2J-K)/k_B T}}.$$

Note that this expression reduces to  $4n_t\mu_0^2/k_B T$  when  $J = K = 0$ , which is the limit of noninteracting spins.

$ \Psi\rangle$	$E$	$ \Psi\rangle$	$E$
$ \uparrow\uparrow\uparrow\uparrow\rangle$	$-6J - K - 4\mu_0H$	$ \uparrow\uparrow\uparrow\downarrow\rangle$	$K - 2\mu_0H$
$ \downarrow\downarrow\downarrow\downarrow\rangle$	$-6J - K + 4\mu_0H$	$ \uparrow\uparrow\downarrow\uparrow\rangle$	$K - 2\mu_0H$
$ \uparrow\uparrow\downarrow\downarrow\rangle$	$2J - K$	$ \uparrow\downarrow\uparrow\uparrow\rangle$	$K - 2\mu_0H$
$ \uparrow\downarrow\uparrow\downarrow\rangle$	$2J - K$	$ \downarrow\downarrow\uparrow\uparrow\rangle$	$K - 2\mu_0H$
$ \uparrow\downarrow\downarrow\uparrow\rangle$	$2J - K$	$ \downarrow\downarrow\uparrow\downarrow\rangle$	$K + 2\mu_0H$
$ \downarrow\downarrow\uparrow\downarrow\rangle$	$2J - K$	$ \uparrow\downarrow\uparrow\uparrow\rangle$	$K + 2\mu_0H$
$ \downarrow\downarrow\downarrow\uparrow\rangle$	$2J - K$	$ \uparrow\uparrow\downarrow\uparrow\rangle$	$K + 2\mu_0H$
$ \downarrow\downarrow\uparrow\uparrow\rangle$	$2J - K$	$ \uparrow\uparrow\uparrow\downarrow\rangle$	$K + 2\mu_0H$

Table 1: Energy table for problem 1.

(2) Look up the relevant parameters for the HCl molecule and find the corresponding value of  $\Theta_{\text{rot}}$ . Then compute the value of the rotational partition function  $\xi_{\text{rot}}(T)$  at  $T = 300$  K, showing the contribution from each of the terms in eqn. 4.266 of the Lecture Notes.

**Solution :**

HCl is a diatomic molecule. Let the separation of the nuclei be  $d$ . From elementary mechanics, the moment of inertia about the CM is  $I = \mu d^2$ , where  $\mu = m_{\text{H}}m_{\text{Cl}}/(m_{\text{H}} + m_{\text{Cl}})$  is the reduced mass. The molar mass of hydrogen is 1 g/mol, while that of chlorine is 35.5 g/mol. Thus,  $\mu = 0.97$  g/mol. I find  $d = 0.13$  nm via web sources. Thus, the temperature associated with rotations is

$$\Theta = \frac{\hbar^2}{2\mu d^2 k_{\text{B}}} = \frac{(1.055 \times 10^{-27} \text{ g cm}^2/\text{s})^2}{2 \cdot (0.97 \text{ g}/6.02 \times 10^{23}) \cdot (1.3 \times 10^{-8} \text{ cm})^2 \cdot 1.38 \times 10^{-16} \text{ erg/K}} = 15 \text{ K}.$$

The rotational partition function is

$$\xi_{\text{rot}} = \int_0^{\infty} dL (2L + 1) e^{-L(L+1)\Theta/T} = \frac{T}{\Theta} + \frac{1}{3} + \frac{1}{15} \frac{\Theta}{T} + \frac{4}{315} \left(\frac{\Theta}{T}\right)^2 + \dots,$$

where  $\Theta = \hbar^2/2Ik_{\text{B}}$ . At  $T = 300$  K,  $\Theta/T = 0.05$ , and the above series yields

$$\xi_{\text{rot}} = 20 + 0.33333 + 0.0033333 + 0.0000317 + \dots = 20.336698 \dots$$

(3) In a chemical reaction among  $\sigma$  species,

$$\zeta_1 A_1 + \zeta_2 A_2 + \dots + \zeta_{\sigma} A_{\sigma} = 0,$$

where  $A_a$  is a chemical formula and  $\zeta_a$  is a stoichiometric coefficient. When  $\zeta_a > 0$ , the corresponding  $A_a$  is a *product*; when  $\zeta_a < 0$ ,  $A_a$  is a *reactant*. (See §2.13.1 of the Lecture Notes.) The condition for equilibrium is

$$\sum_{a=1}^{\sigma} \zeta_a \mu_a = 0,$$

where  $\mu_a$  is the chemical potential of the  $a^{\text{th}}$  species. The *equilibrium constant* for the reaction is defined as

$$\kappa(T, p) = \prod_{a=1}^{\sigma} x_a^{\zeta_a},$$

where  $x_a = n_a / \sum_{b=1}^{\sigma} n_b$  is the fraction of species  $a$ .

(a) Working in the grand canonical ensemble, show that

$$\kappa(T, p) = \prod_{a=1}^{\sigma} \left( \frac{k_B T \xi_a(T)}{p \lambda_a^3} \right)^{\zeta_a}.$$

Note that the above expression does not involve any of the chemical potentials  $\mu_a$ .

(b) Compute the equilibrium constant  $\kappa(T, p)$  for the dissociative reaction  $\text{N}_2 \rightleftharpoons 2\text{N}$  at  $T = 5000\text{ K}$ , assuming the following: the characteristic temperature of rotation and that of vibration of the  $\text{N}_2$  molecule are  $\Theta_{\text{rot}} = 2.84\text{ K}$  and  $\Theta_{\text{vib}} = 3350\text{ K}$ . The dissociation energy, including zero point contributions, is  $\Delta = 169.3\text{ kcal mol}^{-1}$ . The electronic ground state of  $\text{N}_2$  has no degeneracy, but that of the  $\text{N}$  atom is 4 due to electronic spin.

**Solution :**

(a) In the GCE, we have

$$\Omega(T, V, \{\mu_a\}) = -k_B T V \sum_{a=1}^{\sigma} \lambda_a^{-3} e^{\mu_a/k_B T} \xi_a,$$

where  $\lambda_a = (2\pi\hbar^2/m_a k_B T)^{1/2}$  the thermal wavelength for species  $a$  and  $\xi_a(T)$  is the internal coordinate partition function for species  $a$ . We then have

$$n_a = -\frac{1}{V} \left( \frac{\partial \Omega}{\partial \mu_a} \right)_{T, V, \mu_{b \neq a}} = z_a \lambda_a^{-3} \xi_a,$$

where  $z_a = e^{\mu_a/k_B T}$ . OK, so we now define

$$x_a = \frac{n_a}{\sum_{b=1}^{\sigma} n_b} = \frac{z_a \lambda_a^{-3} \xi_a}{p/k_B T} = \frac{k_B T \xi_a z_a}{p \lambda_a^3},$$

since  $\sum_b n_b = -\Omega/V k_B T = p/k_B T$ . (Remember  $\Omega = -pV$ ). Therefore

$$\begin{aligned} \kappa(T, p) &\equiv \prod_{a=1}^{\sigma} x_a^{\zeta_a} \\ &= \prod_{a=1}^{\sigma} \left( \frac{k_B T \xi_a}{p \lambda_a^3} \right)^{\zeta_a} \cdot \prod_{a=1}^{\sigma} z_a^{\zeta_a}. \end{aligned}$$

However,

$$\prod_{a=1}^{\sigma} z_a^{\zeta_a} = \prod_{a=1}^{\sigma} e^{\zeta_a \mu_a / k_B T} = \exp\left(\frac{1}{k_B T} \sum_{a=1}^{\sigma} \zeta_a \mu_a\right) = 1,$$

since  $\sum_{a=1}^{\sigma} \zeta_a \mu_a = 0$ .

(b) The internal partition function for N is just  $\xi_N = (2S + 1)(2I + 1)$ , where  $S = \frac{3}{2}$  is the total electronic spin from Hund's rules, and  $I = 1$  is the nuclear spin. It turns out that we will never need to know the value of  $I$ . For for  $N_2$  the internal partition function is

$$\xi_{N_2} = (2I + 1)^2 \cdot \frac{T}{2\Theta_{\text{rot}}} \cdot \frac{e^{\Delta/T}}{1 - e^{-\Theta_{\text{vib}}/T}}.$$

This formula requires some explanation. We appeal to Eqs. 4.288 and 4.289 in the Lecture Notes. Since  $T \gg \Theta_{\text{rot}}$ , we have

$$\zeta_g \approx \zeta_u \approx \frac{1}{2} \int_0^{\infty} du e^{-u\Theta_{\text{rot}}/T} = \frac{T}{2\Theta_{\text{rot}}},$$

where the factor of  $\frac{1}{2}$  comes from summing only over half the allowed  $L$  values, *i.e.* either all even or all odd, and where  $u = L(L + 1)$  so  $du = (2L + 1) dL$ . We then have  $\xi_{\text{rot}} = (2I + 1)^2 T / 2\Theta_{\text{rot}}$  because  $g_g + g_u = (2I + 1)^2$ . The vibrational partition function was derived to be  $\xi_{\text{vib}} = \frac{1}{2} \text{csch}(\Theta_{\text{vib}}/2T)$ , however since we are including the zero point vibrational energy  $\frac{1}{2}\hbar\omega_{\text{vib}} = \frac{1}{2}k_B\Theta_{\text{vib}}$  in the dissociation energy, we get the above expression for  $\xi_{N_2}$ . According to our result from part (a), we have

$$\begin{aligned} \kappa(T, p) &= 32k_B\Theta_{\text{rot}} \cdot e^{-\Delta/T} \cdot (1 - e^{-\Theta_{\text{vib}}/T}) \cdot \frac{\lambda_{N_2}^3}{p\lambda_N^6} \\ &= 8\sqrt{2} \cdot \frac{k_B\Theta_{\text{rot}}}{p\lambda_N^3} \cdot e^{-\Delta/T} \cdot (1 - e^{-\Theta_{\text{vib}}/T}). \end{aligned}$$

Now we need to evaluate some quantities. The gas constant is

$$R = N_A k_B = 8.314 \text{ J/mol} \cdot \text{K} = 1.986 \times 10^{-3} \text{ kcal/mol} \cdot \text{K},$$

hence at  $T = 5000 \text{ K}$ , we have  $\Delta/k_B T = 17.0$ . Furthermore,  $\Theta_{\text{vib}}/T = 0.670$ . The thermal wavelength of N at this temperature is found to be

$$\lambda_N = \left( \frac{2\pi \cdot (1.055 \times 10^{-27} \text{ g cm}^2/\text{s})^2}{(14 \text{ g}/6.02 \times 10^{23}) \cdot (1.38 \times 10^{-16} \text{ erg/K}) \cdot 5000 \text{ K}} \right)^{1/2} = 6.60 \text{ \AA}.$$

We also have

$$\frac{k_B\Theta_{\text{rot}}}{p\lambda_N^3} = \frac{p_0}{p} \cdot \frac{(1.38 \times 10^{-16} \text{ erg/K}) \cdot (2.84 \text{ K})}{(1.013 \times 10^6 \text{ g/cm} \cdot \text{s}^2)(6.60 \times 10^{-8} \text{ cm})^3} = 1.35 p_0/p,$$

where  $p_0 = 1.013 \times 10^5 \text{ Pa}$  is atmospheric pressure. Putting it all together, we obtain

$$\kappa(T = 5000 \text{ K}, p) = 3.09 \times 10^{-7} \cdot \frac{p_0}{p}.$$

**PHYSICS 140A : STATISTICAL PHYSICS  
HW ASSIGNMENT #6 SOLUTIONS**

(1) A substance obeys the thermodynamic relation  $E = aS^4/VN^2$ .

- (a) Compute the heat capacity  $C_{V,N}$  in terms of  $N$ ,  $V$ , and  $T$ .
- (b) Compute the equation of state relating  $p$ ,  $V$ ,  $N$ , and  $T$ .
- (c) Compute the ratio  $C_{\varphi,N}/C_{V,N}$ , where  $C_{\varphi,N}$  is the heat capacity at constant  $\varphi$  and  $N$ , with  $\varphi = V^2/T$ .

**Solution :**

(a) We have

$$T = \left. \frac{\partial E}{\partial S} \right|_{V,N} = \frac{4aS^3}{VN^2} \Rightarrow S = \left( \frac{TVN^2}{4a} \right)^{1/3} .$$

Plugging this into the expression for  $E(S, V, N)$ , we obtain

$$E(T, V, N) = \frac{1}{4}(4a)^{-1/3} T^{4/3} V^{1/3} N^{2/3} ,$$

and hence

$$C_{V,N} = \left. \frac{\partial E}{\partial T} \right|_{V,N} = \frac{1}{3}(4a)^{-1/3} T^{1/3} V^{1/3} N^{2/3} .$$

(b) We have  $T(S, V, N)$  and so we must find  $p(S, V, N)$  and then eliminate  $S$ . Thus,

$$p = - \left. \frac{\partial E}{\partial V} \right|_{S,N} = \frac{aS^4}{V^2N^2} = \frac{1}{4}(4a)^{-1/3} T^{4/3} V^{-2/3} N^{2/3} .$$

Cubing this result eliminates the fractional powers, yielding the equation of state

$$256a p^3 V^2 = N^2 T^4 .$$

Note also that  $E = pV$  and  $C_{V,N} = 4pV/3T$ .

(d) We have  $dE = \dot{d}Q - p dV$ , so

$$\dot{d}Q = dE + p dV = C_{V,N} dT + \left\{ \left( \frac{\partial E}{\partial V} \right)_{T,N} + p \right\} dV .$$

Now we need to compute  $dV|_{\varphi,N}$ . We write

$$d\varphi = -\frac{V^2}{T^2} dT + \frac{2V}{T} dV ,$$

hence

$$dV|_{\varphi,N} = \frac{V}{2T} dT .$$

Substituting this into our expression for  $dQ$ , we have

$$C_{\varphi,N} = C_{V,N} + \left\{ \left( \frac{\partial E}{\partial V} \right)_{T,N} + p \right\} \frac{V}{2T}.$$

It is now left to us to compute

$$\left( \frac{\partial E}{\partial V} \right)_{T,N} = \frac{1}{12} (4a)^{-1/3} T^{4/3} V^{-2/3} N^{2/3} = \frac{1}{3} p.$$

We then have

$$C_{\varphi,N} = C_{V,N} + \frac{2pV}{3T} = \frac{3}{2} C_{V,N}.$$

Thus,

$$\frac{C_{\varphi,N}}{C_{V,N}} = \frac{3}{2}.$$

(2) Consider an engine cycle which follows the thermodynamic path in Fig. 1. The work material is  $\nu$  moles of a diatomic ideal gas. BC is an isobar ( $dp = 0$ ), CA is an isochore ( $dV = 0$ ), and along AB one has

$$p(V) = p_B + (p_A - p_B) \cdot \sqrt{\frac{V_B - V}{V_B - V_A}}.$$

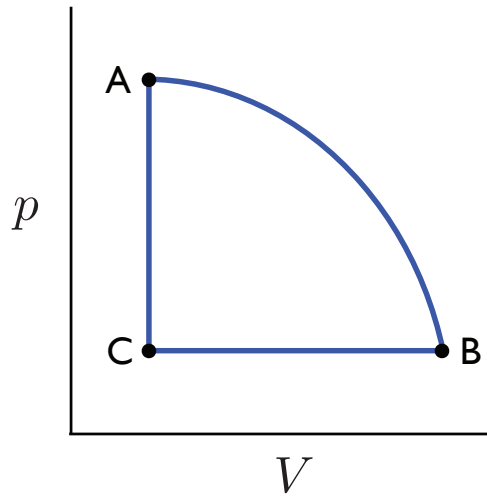


Figure 1: Thermodynamic path for problem 2.

- (a) Find the heat acquired  $Q_{AB}$  and the work done  $W_{AB}$ .
- (b) Find the heat acquired  $Q_{BC}$  and the work done  $W_{BC}$ .

(c) Find the heat acquired  $Q_{CA}$  and the work done  $W_{CA}$ .

(d) Find the work  $W$  done per cycle.

**Solution :**

Note that  $p_C = p_B$  and  $V_C = V_A$ , so we will only need to use  $\{p_A, p_B, V_A, V_B\}$  in our analysis. For a diatomic ideal gas,  $E = \frac{5}{2}pV$ .

(a) We first compute the work done along AB. Let's define  $u$  such that  $V = V_A + (V_B - V_A)u$ . Then along AB we have  $p = p_B + (p_A - p_B)\sqrt{1-u}$ , and

$$\begin{aligned}W_{AB} &= \int_A^B dV p \\&= (V_B - V_A) \int_0^1 du \left\{ p_B + (p_A - p_B)\sqrt{1-u} \right\} \\&= p_B(V_B - V_A) + \frac{2}{3}(V_B - V_A)(p_A - p_B).\end{aligned}$$

The change in energy along AB is

$$(\Delta E)_{AB} = E_B - E_A = \frac{5}{2}(p_B V_B - p_A V_A),$$

hence

$$\begin{aligned}Q_{AB} &= (\Delta E)_{AB} + W_{AB} \\&= \frac{5}{6}p_B V_B - \frac{19}{6}p_A V_A + \frac{2}{3}p_A V_B + \frac{5}{3}p_B V_A.\end{aligned}$$

(b) Along BC we have

$$W_{BC} = p_B(V_A - V_B)$$

$$(\Delta E)_{BC} = \frac{5}{2}p_B(V_A - V_B)$$

$$Q_{BC} = (\Delta E)_{BC} - W_{BC} = \frac{3}{2}p_B(V_A - V_B).$$

(c) Along CA we have

$$W_{CA} = 0$$

$$(\Delta E)_{CA} = \frac{5}{2}(p_A - p_B)V_A$$

$$Q_{CA} = (\Delta E)_{CA} - W_{CA} = \frac{5}{2}(p_A - p_B)V_A.$$



(c) The work done per cycle is

$$\begin{aligned} W &= W_{AB} + W_{BC} + W_{CA} \\ &= \frac{2}{3}(V_B - V_A)(p_A - p_B). \end{aligned}$$

**(3)** For each of the following differentials, determine whether it is exact or inexact. If it is exact, find the function whose differential it represents.

(a)  $xy^2 dx + x^2y dy$

(b)  $z dx + x dy + y dz$

(c)  $x^{-2} dx - 2x^{-3} dy$

(d)  $e^x dx + \ln(y) dy$

**Solution :**

We will represent each differential as  $dA = \sum_{\mu} A_{\mu} dx^{\mu}$ .

(a)  $A_x = xy^2$  and  $A_y = x^2y$ , so  $\frac{\partial A_x}{\partial y} = 2xy = \frac{\partial A_y}{\partial x}$ . The differential is exact, and is  $dA$ , where  $A(x, y) = \frac{1}{2}x^2y^2 + C$ , where  $C$  is a constant.

(b) With  $A_x = z$ ,  $A_y = x$ , and  $A_z = y$ , we have  $\frac{\partial A_x}{\partial y} = 0 = \frac{\partial A_y}{\partial x}$ , but  $\frac{\partial A_x}{\partial z} = 1 \neq \frac{\partial A_z}{\partial x} = 0$ . So the differential is inexact.

(c)  $A_x = x^{-2}$  and  $A_y = -2x^{-3}$ , so  $\frac{\partial A_x}{\partial y} = -2x^{-3}$  and  $\frac{\partial A_y}{\partial x} = 0$ , so the differential is inexact.

(d)  $A_x = e^x$  and  $A_y = \ln y$ , so  $\frac{\partial A_x}{\partial y} = 0 = \frac{\partial A_y}{\partial x} = 0$ . The differential is exact, with  $A(x, y) = e^x + y \ln y - y + C$ .

**PHYSICS 140A : STATISTICAL PHYSICS**  
**HW ASSIGNMENT #7**

(1) A strange material satisfies  $E(S, V, N) = a S^6 / V^3 N^2$ .

- (a) What are the SI dimensions of  $a$ ?
- (b) Find the equation of state relating  $p$ ,  $T$ , and  $n = N/V$ .
- (c) Find the coefficient of thermal expansion  $\alpha_p = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p$ . Express your answer in terms of  $T$ .
- (d) Find the coefficient of isothermal compressibility  $\kappa_T = -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_T$ . Express your answer in terms of  $p$ .

**Solution :**

(a) Since  $[S] = \text{J/K}$ , we have  $[a] = \text{K}^6 \text{m}^9 / \text{J}^5$ .

(b) We have

$$T = \left( \frac{\partial E}{\partial S} \right)_{V,N} = \frac{6aS^5}{V^3 N^2} \quad , \quad p = - \left( \frac{\partial E}{\partial V} \right)_{S,N} = \frac{3aS^6}{V^4 N^2} .$$

The combination  $T^6/p^5$  eliminates  $S$ , and we obtain the equation of state,

$$192a p^5 V^2 = N^2 T^6 .$$

(c) At constant  $p$  and  $N$ , we have  $\ln V = 3 \ln T + \text{const}$ . Thus, the coefficient of thermal expansion is

$$\alpha_p = \left( \frac{\partial \ln V}{\partial T} \right)_{p,N} = \frac{3}{T} .$$

(d) At constant  $T$  and  $N$ , we have  $\ln V = -\frac{5}{2} \ln p + \text{const}$ . Thus, the isothermal compressibility is

$$\kappa_T = - \left( \frac{\partial \ln V}{\partial p} \right)_{T,N} = \frac{5}{2p} .$$

(2)  $\nu$  moles of the substance in problem 1 execute a Carnot cycle between reservoirs at temperatures  $T_1$  and  $T_2$ . The top isotherm extends from volume  $V_A$  to  $V_B$ . Find the heat  $Q$  and work  $W$  for each leg of the cycle, and compute the cycle efficiency.

**Solution :**

It is useful to use §2.7.6 of the Lecture Notes as a template. From the results of problem (1), we have

$$E = \frac{1}{3}pV = \frac{1}{3} \left( \frac{N^2 V^3 T^6}{192a} \right)^{1/5}.$$

Thus, under isothermal conditions,

$$dE|_T = \frac{1}{5} \left( \frac{N^2 T^6}{192a} \right)^{1/5} \frac{dV}{V^{2/5}} = \frac{1}{5} p dV.$$

Thus, along an isotherm, we have

$$W_{\text{if}} = \int_{V_i}^{V_f} dV p = 5(E_f - E_i)$$

$$Q_{\text{if}} = E_f - E_i + W_{\text{if}} = 6(E_f - E_i).$$

Along an adiabat, we have  $TV^3 = \text{const.}$  and  $E/T = \text{const.}$ , so

$$E_B = \left( \frac{V_B}{V_A} \right)^{3/5} E_A, \quad E_C = \frac{T_1}{T_2} \left( \frac{V_B}{V_A} \right)^{3/5} E_A, \quad E_D = \frac{T_1}{T_2} E_A,$$

where AB is an isotherm at  $T_2$ , BC is an adiabat, CD is an isotherm at  $T_1$ , and DA is an adiabat. We now have

$$W_{\text{AB}} = 5(E_B - E_A) = 5 \left\{ \left( \frac{V_B}{V_A} \right)^{3/5} - 1 \right\} E_A$$

$$Q_{\text{AB}} = 6(E_B - E_A) = 6 \left\{ \left( \frac{V_B}{V_A} \right)^{3/5} - 1 \right\} E_A$$

$$W_{\text{BC}} = E_C - E_B = \left( 1 - \frac{T_1}{T_2} \right) \left( \frac{V_B}{V_A} \right)^{3/5} E_A$$

$$Q_{\text{BC}} = 0$$

and

$$W_{\text{CD}} = 5(E_D - E_C) = 5 \frac{T_1}{T_2} \left\{ 1 - \left( \frac{V_B}{V_A} \right)^{3/5} \right\} E_A$$

$$Q_{\text{CD}} = 6(E_D - E_C) = 6 \frac{T_1}{T_2} \left\{ 1 - \left( \frac{V_B}{V_A} \right)^{3/5} \right\} E_A$$

$$W_{\text{DA}} = E_A - E_D = \left( \frac{T_1}{T_2} - 1 \right) E_A$$

$$Q_{\text{DA}} = 0$$

Adding up the work along the four legs of the Carnot cycle, we have

$$W = 6 \left( 1 - \frac{T_1}{T_2} \right) \left\{ \left( \frac{V_B}{V_A} \right)^{3/5} - 1 \right\} E_A ,$$

and the efficiency is

$$\eta = \frac{W}{Q_{AB}} = 1 - \frac{T_1}{T_2} ,$$

which is the same result as for an ideal gas. Were the efficiency different from that of the ideal gas Carnot cycle running between the same two reservoirs, one could use one of the engines to drive the other run as a refrigerator and thereby violate the Second Law of Thermodynamics, *i.e.* transferring heat from the cold reservoir to the warm reservoir during a cycle. The fact that this is impossible requires that the efficiencies are exactly the same.

(3) An interacting diatomic gas obeys the equation of state

$$p(v - b) = RT e^{-a/v} ,$$

where  $v = N_A V / N$  is the molar volume.

(a) Show that  $E(T, V, N) = \frac{f}{2} N k_B T$ , the same as for an ideal gas.

(b) Find the molar specific heat  $c_p$  as a function of the specific volume  $v$ .

**Solution :**

(a) We know that

$$\left( \frac{\partial \varepsilon}{\partial v} \right)_T = T \left( \frac{\partial p}{\partial T} \right)_v - p ,$$

where  $\varepsilon$  and  $v$  are molar energy and molar volume, respectively. For our system, the RHS of the above equation vanishes, hence  $\varepsilon = \varepsilon(T)$ . In the dilute limit we know the answer, and since  $\varepsilon$  is independent of volume, this is true for arbitrary molar volumes. Thus,  $\varepsilon(T) = \frac{1}{2} f RT$ , *i.e.*  $E = \frac{1}{2} f N k_B T$ .

(b) We have

$$c_p = T \left( \frac{\partial s}{\partial T} \right)_p = \left( \frac{\partial \varepsilon}{\partial T} \right)_p + p \left( \frac{\partial v}{\partial T} \right)_p .$$

The first term on the RHS yields  $\frac{1}{2} f R$ . To evaluate the second term, we appeal to the equation of state at constant pressure, which yields, upon taking the differential,

$$\begin{aligned} p dv &= R e^{-a/v} dT + \frac{RTa}{v^2} e^{-a/v} dv \\ &= \frac{RT}{v-b} e^{-a/v} dv . \end{aligned}$$

Thus,

$$\left(\frac{\partial v}{\partial T}\right)_p = \frac{v - b}{T - \frac{Ta(v-b)}{v^2}}.$$

We then have

$$c_p = \frac{1}{2}fR + \frac{Re^{-a/v}}{1 - \frac{a(v-b)}{v^2}}.$$

Note that  $c_p(v \rightarrow \infty) = (\frac{1}{2}f + 1)R$ , which is the ideal gas value.

**PHYSICS 140A : STATISTICAL PHYSICS**  
**HW ASSIGNMENT #8 SOLUTIONS**

**(1)** A grocer starts his day with 4 boxes of pears, 5 boxes of oranges, and 6 boxes of apples. Each box contains 24 fruit and is initially completely filled.

- (a) At some time, the grocer notes that exactly half the pears, a third of the oranges, and a quarter of the apples have been sold. Assuming that customers take fruit from random positions in each of the boxes, find the dimensionless entropy  $\ln W$  of the fruit distribution.
- (b) A clumsy customer then topples the table on which the fruit boxes rest, and all the fruit fall to the ground. The customer cleans up the mess, putting all the fruit back into the boxes, but into random locations. What is the entropy of the final state?

**Solution :**

(a) The grocer starts with 96 pears, 120 oranges, and 144 apples. By the time the grocer checks, 48 pears, 40 oranges, and 36 apples have been removed. The number of ways of doing this is

$$W = \binom{96}{48} \binom{120}{40} \binom{144}{36} = 8.303 \times 10^{93} .$$

Thus,  $\ln W = 216.3$ .

(b) There are a total of  $96 + 120 + 144 = 360$  slots for the fruit, which contain the remaining 48 pears, 120 oranges, and 108 apples. The rest of the slots, which amount to  $360 - 48 - 120 - 108 = 84$  in total, are empty. Therefore,

$$W' = \frac{360!}{94! \cdot 48! \cdot 120! \cdot 108!} = 1.093 \times 10^{205} ,$$

and the dimensionless entropy is  $\ln W' = 472.1$ .

**(2)** The *triple point* of a single component thermodynamic system is an isolated point  $(T_t, p_t)$  in the  $(T, p)$  plane where there is three phase coexistence between solid, liquid, and vapor. Consider three phase coexistence between a pure solid, a pure vapor, and a solution where the solute fraction is  $x$ . Find the shift  $(\Delta T_t, \Delta p_t)$  as a function of  $x, T_t$ , and the quantities  $s_{S,L,V}$  and  $v_{S,L,V}$ , *i.e.* the molar entropies and volumes of the three respective phases.

**Solution :**

At the triple point, we have  $\mu_S(T_t, p_t) = \mu_L(T_t, p_t) = \mu_V(T_t, p_t)$ , which gives two equations for the two unknowns  $T_t$  and  $p_t$ . We write  $T_t = T_t^0 + \Delta T$  and  $p_t = p_t^0 + \Delta p$ , and we solve

$$\begin{aligned} \mu_L^0(T_t^0 + \Delta T, p_t^0 + \Delta p) - x k_B (T_t^0 + \Delta T) &= \mu_V^0(T_t^0 + \Delta T, p_t^0 + \Delta p) \\ \mu_V^0(T_t^0 + \Delta T, p_t^0 + \Delta p) &= \mu_S^0(T_t^0 + \Delta T, p_t^0 + \Delta p) , \end{aligned}$$

where the 0 superscript indicates the value for a pure phase. We now expand in the notionally small quantities  $\Delta T$  and  $\Delta p$ , and we use

$$\left(\frac{\partial\mu}{\partial T}\right)_{p,N} = -\left(\frac{\partial S}{\partial N}\right)_{p,T} = -\frac{s}{N_A} \quad , \quad \left(\frac{\partial\mu}{\partial p}\right)_{T,N} = \left(\frac{\partial V}{\partial N}\right)_{p,T} = \frac{v}{N_A} ,$$

where  $s$  and  $v$  are the molar entropy and molar volume, respectively. This yields the linear system,

$$\begin{pmatrix} s_V - s_L & v_L - v_V \\ s_S - s_V & v_V - v_S \end{pmatrix} \begin{pmatrix} \Delta T \\ \Delta p \end{pmatrix} = \begin{pmatrix} xRT_t^0 \\ 0 \end{pmatrix} .$$

This yields

$$\Delta T = \frac{(v_V - v_S) \cdot xRT_t^0}{s_V(v_L - v_S) + s_L(v_S - v_V) + s_S(v_V - v_L)}$$

$$\Delta p = \frac{(s_V - s_S) \cdot xRT_t^0}{s_V(v_L - v_S) + s_L(v_S - v_V) + s_S(v_V - v_L)} .$$

Note that we do not retain terms of order  $x \Delta T$ , because we have assumed  $x$  is small, *i.e.* a weak solution.

**(3)** A solution of 4.00 g of hemoglobin in 100 mL of water was prepared and its osmotic pressure was measured to be  $\pi = 0.0130$  atm at  $T = 280$  K. Estimate the molecular mass of hemoglobin.

**Solution :**

We use the formula  $\pi v = xRT$  for the osmotic pressure  $\pi$  of weak solutions. Here  $v$  is the molar volume of the solvent, and  $x$  is the molar fraction of solute. If  $M$  is the molar mass of hemoglobin, then

$$x = \frac{4.00 \text{ g}}{M} \bigg/ \frac{100 \text{ g}}{18 \text{ g}} = \frac{18 \text{ g}}{25 M} ,$$

since the density of water is  $1.0 \text{ g/cm}^3 = 1 \text{ g/mL}$ . We then have

$$M = \frac{18}{25} \text{ g} \cdot \frac{RT}{\pi v}$$

$$= \frac{18 \text{ g}}{25} \cdot \frac{(8.314 \times 10^7 \text{ erg/mol K})(280 \text{ K})}{(0.013 \text{ atm})(1.013 \times 10^6 \text{ g/cm}^2 \text{ atm})(18 \text{ cm}^3/\text{mol})} = 70710 \text{ g} .$$

The actual value is  $M = 65706 \text{ g}$ .

**PHYSICS 140A : STATISTICAL PHYSICS  
HW #9 SOLUTIONS**

**(1)** Consider a three-dimensional gas of noninteracting quantum particles with dispersion  $\varepsilon(\mathbf{k}) = A |\mathbf{k}|^{3/2}$ .

- (a) Find the single particle density of states per unit volume  $g(\varepsilon)$ .
- (b) Find expressions for  $n(T, z)$  and  $p(T, z)$ , each expressed as power series in the fugacity  $z$ , for both Bose-Einstein and Fermi-Dirac statistics.
- (c) Find the virial expansion for the equation of state up to terms of order  $n^3$ , for both bosons and fermions.

**Solution :**

(a) The density of states for dispersion  $\varepsilon(\mathbf{k}) = A |\mathbf{k}|^\sigma$  is

$$\begin{aligned} g(\varepsilon) &= g \int \frac{d^d k}{(2\pi)^d} \delta(\varepsilon - Ak^\sigma) \\ &= \frac{g \Omega_d}{(2\pi)^d} \int_0^\infty dk k^{d-1} \frac{\delta(k - (\varepsilon/A)^{1/\sigma})}{\sigma A k^{\sigma-1}} = D \varepsilon^{\frac{d}{\sigma}-1}, \end{aligned}$$

with

$$D = \frac{2g}{(2\sqrt{\pi})^d \sigma \Gamma(d/2)} A^{-d/\sigma}.$$

(b) We have

$$\begin{aligned} n(T, z) &= \sum_{j=1}^{\infty} (\pm 1)^{j-1} C_j(T) z^j \\ p(T, z) &= k_B T \sum_{j=1}^{\infty} (\pm 1)^{j-1} z^j j^{-1} C_j(T) z^j, \end{aligned}$$

where

$$C_j(T) = \int_{-\infty}^{\infty} d\varepsilon g(\varepsilon) e^{-j\varepsilon/k_B T} = D \Gamma(d/\sigma) \left( \frac{k_B T}{j} \right)^{d/\sigma}.$$

Thus, we have

$$\begin{aligned} \pm n v_T &= \sum_{j=1}^{\infty} j^{-r} (\pm z)^j \\ \pm p v_T / k_B T &= \sum_{j=1}^{\infty} j^{-(r+1)} (\pm z)^j, \end{aligned}$$



where  $r = d/\sigma$  and

$$v_T = \frac{1}{D\Gamma(d/\sigma)(k_B T)^{d/\sigma}} = \frac{(2\sqrt{\pi})^d \sigma \Gamma(d/2)}{2g D\Gamma(d/\sigma)} \left(\frac{A}{k_B T}\right)^{d/\sigma}.$$

has dimensions of volume.

(c) We now let  $x = \pm z$ , and interrogate Mathematica:

```
In[1]= y = InverseSeries[x + x^2/2^r + x^3/3^r + x^4/4^r + O[x]^5]
```

```
In[2]= w = y + y^2/2^(r+1) + y^3/3^(r+1) + y^4/4^(r+1) + O[y]^5.
```

The result is

$$p = nk_B T \left[ 1 + B_2(T) n + B_3(T) n^2 + \dots \right],$$

where

$$B_2(T) = \mp 2^{-(r+1)} v_T$$

$$B_3(T) = \left( 2^{-2r} - 2 \cdot 3^{-(r+1)} \right) v_T^2$$

$$B_4(T) = \pm 2^{-(3r+1)} 3^{1-r} \left( 2^{2r+1} - 5 \cdot 3^{r-1} - 2^{r-1} 3^r \right) v_T^3.$$

Substitute  $\sigma = \frac{3}{2}$  to find the solution for the conditions given.

**(2)** You know that at most one fermion may occupy any given single-particle state. A *parafermion* is a particle for which the maximum occupancy of any given single-particle state is  $k$ , where  $k$  is an integer greater than zero. (For  $k = 1$ , parafermions are regular everyday fermions; for  $k = \infty$ , parafermions are regular everyday bosons.) Consider a system with one single-particle level whose energy is  $\varepsilon$ , *i.e.* the Hamiltonian is simply  $\mathcal{H} = \varepsilon n$ , where  $n$  is the particle number.

- (a) Compute the partition function  $\Xi(\mu, T)$  in the grand canonical ensemble for parafermions.
- (b) Compute the occupation function  $n(\mu, T)$ . What is  $n$  when  $\mu = -\infty$ ? When  $\mu = \varepsilon$ ? When  $\mu = +\infty$ ? Does this make sense? Show that  $n(\mu, T)$  reduces to the Fermi and Bose distributions in the appropriate limits.
- (c) Sketch  $n(\mu, T)$  as a function of  $\mu$  for both  $T = 0$  and  $T > 0$ .

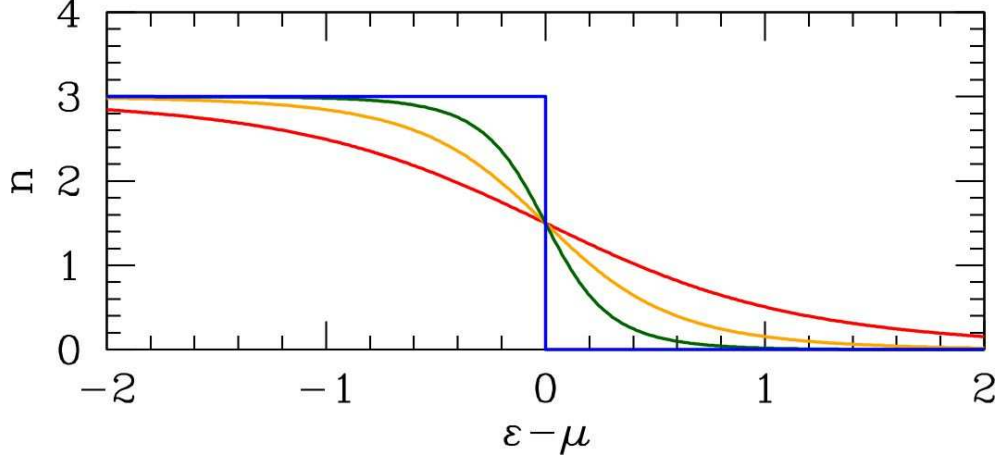


Figure 1:  $k = 3$  parafermion occupation number *versus*  $\varepsilon - \mu$  for  $k_B T = 0$ ,  $k_B T = 0.25$ ,  $k_B T = 0.5$ , and  $k_B T = 1$ . (Problem 2b)

**Solution:**

The general expression for  $\Xi$  is

$$\Xi = \prod_{\alpha} \sum_{n_{\alpha}} (z e^{-\beta \varepsilon_{\alpha}})^{n_{\alpha}} .$$

Now the sum on  $n$  runs from 0 to  $k$ , and

$$\sum_{n=0}^k x^n = \frac{1 - x^{k+1}}{1 - x} .$$

(a) Thus,

$$\Xi = \frac{1 - e^{(k+1)\beta(\mu-\varepsilon)}}{1 - e^{\beta(\mu-\varepsilon)}} .$$

(b) We then have

$$\begin{aligned} n &= -\frac{\partial \Omega}{\partial \mu} = \frac{1}{\beta} \frac{\partial \ln \Xi}{\partial \mu} \\ &= \frac{1}{e^{\beta(\varepsilon-\mu)} - 1} - \frac{k+1}{e^{(k+1)\beta(\varepsilon-\mu)} - 1} \end{aligned}$$

(c) A plot of  $n(\varepsilon, T, \mu)$  for  $k = 3$  is shown in Fig. 1. Qualitatively the shape is that of the Fermi function  $f(\varepsilon - \mu)$ . At  $T = 0$ , the occupation function is  $n(\varepsilon, T = 0, \mu) = k \Theta(\mu - \varepsilon)$ . This step function smooths out for  $T$  finite.

(d) For each  $k < \infty$ , the occupation number  $n(z, T)$  is a finite order polynomial in  $z$ , and hence an analytic function of  $z$ . Therefore, there is no possibility for Bose condensation except for  $k = \infty$ .

(3) A gas of quantum particles with photon statistics has dispersion  $\varepsilon(\mathbf{k}) = A |\mathbf{k}|^4$ .

- (a) Find the single particle density of states per unit volume  $g(\varepsilon)$ .
- (b) Repeat the arguments of §5.5.2 in the Lecture Notes for this dispersion.
- (c) Assuming our known values for the surface temperature of the sun, the radius of the earth-sun orbit, and the radius of the earth, what would you expect the surface temperature of the earth to be if the sun radiated particles with this dispersion instead of photons?

**Solution :**

(a) See the solution to part (a) of problem 1 above. For  $d = 3$  and  $\sigma = 4$  we have

$$g(\varepsilon) = \frac{\mathfrak{g}}{2\pi^2} A^{-3/4} \varepsilon^{-1/4} .$$

(b) Scaling volume by  $\lambda$  scales the lengths by  $\lambda^{1/3}$ , the quantized wavevectors by  $\lambda^{-1/3}$ , and the energy eigenvalues by  $\lambda^{-4/3}$ , since  $\varepsilon \propto k^4$ . Thus,

$$p = - \left( \frac{\partial E}{\partial V} \right)_S = \frac{4E}{3V} ,$$

which says

$$\left( \frac{\partial E}{\partial V} \right)_T = T \left( \frac{\partial p}{\partial T} \right)_V - p = \frac{3}{4} p \quad \Rightarrow \quad p(T) = B T^{7/4} .$$

Indeed,

$$\begin{aligned} p(T) &= -k_B T \int_{-\infty}^{\infty} g(\varepsilon) \ln(1 - e^{-\varepsilon/k_B T}) \\ &= -\frac{\mathfrak{g}}{2\pi^2} A^{3/4} (k_B T)^{7/4} \int_{-\infty}^{\infty} du u^{-1/4} \ln(1 - e^{-u}) . \end{aligned}$$

(c) See §5.5.5 of the Lecture Notes. Assume a dispersion of the form  $\varepsilon(k)$  for the (non-conserved) bosons. Then the energy current incident on a differential area  $dA$  of surface normal to  $\hat{z}$  is

$$dP = dA \cdot \int \frac{d^3k}{(2\pi)^3} \Theta(\cos \theta) \cdot \varepsilon(k) \cdot \frac{1}{\hbar} \frac{\partial \varepsilon(k)}{\partial k_z} \cdot \frac{1}{e^{\varepsilon(k)/k_B T} - 1} .$$

Note that

$$\frac{\partial \varepsilon(k)}{\partial k_z} = \frac{k_z}{k} \frac{\partial \varepsilon}{\partial k} = \cos \theta \varepsilon'(k).$$

Now let us assume a power law dispersion  $\varepsilon(k) = Ak^\alpha$ . Changing variables to  $t = Ak^\alpha/k_B T$ , we find

$$\frac{dP}{dA} = \sigma T^{2+\frac{2}{\alpha}},$$

where

$$\sigma = \zeta\left(2 + \frac{2}{\alpha}\right) \Gamma\left(2 + \frac{2}{\alpha}\right) \cdot \frac{g k_B^{2+\frac{2}{\alpha}} A^{-\frac{2}{\alpha}}}{8\pi^2 \hbar}.$$

One can check that for  $g = 2$ ,  $A = \hbar c$ , and  $\alpha = 1$  that this result reduces to Stefan's Law.

Equating the power incident on the earth to that radiated by the earth,

$$4\pi R_\odot^2 \cdot \sigma T_\odot^{2(1+\alpha^{-1})} \cdot \frac{\pi R_e^2}{4\pi a_e^2} = 4\pi R_e^2 \cdot \sigma T_e^{2(1+\alpha^{-1})},$$

which yields

$$T_e = \left(\frac{R_\odot}{2a_e}\right)^{\frac{\alpha}{\alpha+1}} T_\odot.$$

Plugging in the appropriate constants and setting  $\alpha = 4$ , we obtain  $T_e = 45.2$  K. Brrr!

**PHYSICS 140A : STATISTICAL PHYSICS  
MIDTERM EXAMINATION SOLUTIONS**

(1) A particle has a  $g_0$ -fold degenerate ground state with energy  $\varepsilon_0 = 0$  and a  $g_1$ -fold degenerate excited state with energy  $\varepsilon_1 = \Delta$ . A collection of  $N$  such particles is arranged on a lattice. Since each particle occupies a distinct position in space, the particles are regarded as distinguishable.

- (a) Find the free energy  $F(T, N)$ .
- (b) Find the entropy  $S(T, N)$ . Sketch  $S(T, N)$  versus  $T$  for fixed  $N$ , taking care to evaluate the limiting values  $S(T = 0, N)$  and  $S(T = \infty, N)$ .

Suppose now that the ground state is magnetic, such that in an external field  $H$ , the  $g_0$  ground state energy levels are split into  $g_0/2$  levels with energy  $\varepsilon_{0,+} = +\mu_0 H$  and  $g_0/2$  levels with energy  $\varepsilon_{0,-} = -\mu_0 H$ . (We take  $g_0$  to be even in this case.) The states with energy  $\varepsilon_1 = \Delta$  remain  $g_1$ -fold degenerate.

- (c) Find  $F(T, N, H)$ .
- (d) Find the zero field magnetic susceptibility,

$$\chi(T) = \frac{1}{N} \left( \frac{\partial M}{\partial H} \right)_{H=0},$$

where  $M$  is the magnetization.

**Solution :**

(a) We have

$$Z(T, N) = (g_0 + g_1 e^{-\beta\Delta})^N,$$

hence

$$\begin{aligned} F(T, N) &= -k_B T \ln Z \\ &= -N k_B T \ln(g_0 + g_1 e^{-\Delta/k_B T}). \end{aligned}$$

(b) The entropy is

$$S = - \left( \frac{\partial F}{\partial T} \right)_N = N k_B \left[ \frac{\Delta}{k_B T} \cdot \frac{g_1 e^{-\Delta/k_B T}}{g_0 + g_1 e^{-\Delta/k_B T}} + \ln(g_0 + g_1 e^{-\Delta/k_B T}) \right].$$

From this we see that  $S(T = 0, N) = N k_B \ln g_0$  and  $S(T = \infty, N) = N k_B \ln(g_0 + g_1)$ , which makes physical sense. The sketch should show a smooth interpolation between these values as a function of  $T$ .

(c) Now we have

$$F(T, N, H) = -Nk_B T \ln \left( g_0 \cosh(\mu_0 H / k_B T) + g_1 e^{-\Delta / k_B T} \right).$$

(d) The magnetization is

$$M(T, H) = - \left( \frac{\partial F}{\partial H} \right)_{T, N} = \frac{N \mu_0 g_0 \sinh(\mu_0 H / k_B T)}{g_0 \cosh(\mu_0 H / k_B T) + g_1 e^{-\Delta / k_B T}}.$$

Taking the derivative and setting  $H = 0$ , we have

$$\chi(T) = \frac{1}{N} \left( \frac{\partial M}{\partial H} \right)_{T, N, H=0} = \frac{\mu_0^2}{k_B T} \cdot \frac{g_0}{g_0 + g_1 e^{-\Delta / k_B T}}.$$

**PHYSICS 140A : STATISTICAL PHYSICS  
FINAL EXAMINATION SOLUTIONS**

**Instructions:** Do problem 4 (34 points) and any two of problems 1, 2, and 3 (33 points each)

(1) A noninteracting system consists of  $N$  dimers. Each dimer consists of two spins,  $S$  and  $\sigma$ , where  $S \in \{-1, 0, +1\}$  and  $\sigma \in \{-1, +1\}$ . The Hamiltonian is

$$\hat{H} = -J \sum_{i=1}^N S_i \sigma_i - \mu_0 H \sum_{i=1}^N S_i.$$

Thus, the individual dimer Hamiltonian is  $\hat{h} = -JS\sigma - \mu_0 HS$ .

(a) Find the  $N$ -dimer free energy  $F(T, N)$ .

(b) Find the average  $\langle S \rangle$  and the zero field susceptibility  $\chi_S(T) = \left. \frac{\partial \langle S \rangle}{\partial H} \right|_{H=0}$ .

(c) Find the average  $\langle \sigma \rangle$  and the zero field susceptibility  $\chi_\sigma(T) = \left. \frac{\partial \langle \sigma \rangle}{\partial H} \right|_{H=0}$ .

(d) Examine the  $J \rightarrow 0$  limits of  $\chi_S(T)$  and  $\chi_\sigma(T)$  and interpret your results physically.

**Solution :**

(a) There are six energy states for each dimer, listed in Tab. 1

$S$	$\sigma$	$\hat{h}(S, \sigma)$	$S$	$\sigma$	$\hat{h}(S, \sigma)$
+1	+1	$-J - \mu_0 H$	+1	-1	$J - \mu_0 H$
0	+1	0	0	-1	0
-1	+1	$+J + \mu_0 H$	-1	-1	$-J + \mu_0 H$

Table 1: Energy table for problem 1.

Thus, the single dimer partition function is

$$\begin{aligned} \zeta &= \text{Tr} e^{-\beta \hat{h}} = e^{\beta J} e^{\beta \mu_0 H} + 1 + e^{-\beta J} e^{-\beta \mu_0 H} + e^{-\beta J} e^{\beta \mu_0 H} + 1 + e^{\beta J} e^{-\beta \mu_0 H} \\ &= 2 + 4 \cosh(\beta \mu_0 J) \cosh(\beta \mu_0 H). \end{aligned}$$

For  $N$  noninteracting dimers,  $Z = \zeta^N$  (the dimers are regarded as distinguishable). Thus,

$$F(T, N) = -N k_B T \ln \left( 2 + 4 \cosh(J/k_B T) \cosh(\mu_0 H/k_B T) \right)$$

(b) We have

$$\langle S \rangle = \frac{\text{Tr} S e^{-\beta \hat{h}(S, \sigma)}}{\text{Tr} e^{-\beta \hat{h}(S, \sigma)}} = \frac{e^{\beta J} e^{\beta \mu_0 H} - e^{-\beta J} e^{-\beta \mu_0 H} + e^{-\beta J} e^{\beta \mu_0 H} - e^{\beta J} e^{-\beta \mu_0 H}}{2 + 4 \cosh(\beta J) \cosh(\beta H)},$$

so

$$\langle S \rangle = \frac{\cosh(J/k_B T) \sinh(\mu_0 H/k_B T)}{\cosh(J/k_B T) \cosh(\mu_0 H/k_B T) + \frac{1}{2}}$$

Expanding to linear order in  $H$  and taking the coefficient, we have

$$\chi_S(T) = \left. \frac{\partial \langle S \rangle}{\partial H} \right|_{H=0} = \frac{\cosh(J/k_B T)}{\cosh(J/k_B T) + \frac{1}{2}} \cdot \frac{\mu_0}{k_B T}$$

Note that usually we define  $\chi = \frac{\partial M}{\partial T}$  with  $M = \mu_0 \langle S \rangle$ , so our result above differs by a factor of  $\mu_0$ .

(c) We have

$$\langle \sigma \rangle = \frac{\text{Tr } \sigma e^{-\beta \hat{h}(S, \sigma)}}{\text{Tr } e^{-\beta \hat{h}(S, \sigma)}} = \frac{e^{\beta J} e^{\beta \mu_0 H} + e^{-\beta J} e^{-\beta \mu_0 H} - e^{-\beta J} e^{\beta \mu_0 H} - e^{\beta J} e^{-\beta \mu_0 H}}{2 + 4 \cosh(\beta J) \cosh(\beta H)},$$

so

$$\langle \sigma \rangle = \frac{\sinh(J/k_B T) \sinh(\mu_0 H/k_B T)}{\cosh(J/k_B T) \cosh(\mu_0 H/k_B T) + \frac{1}{2}}$$

Expanding to linear order in  $H$  and taking the coefficient, we have

$$\chi_\sigma(T) = \left. \frac{\partial \langle \sigma \rangle}{\partial H} \right|_{H=0} = \frac{\sinh(J/k_B T)}{\cosh(J/k_B T) + \frac{1}{2}} \cdot \frac{\mu_0}{k_B T}$$

(d) As  $J \rightarrow 0$  we have

$$\chi_S(T, J=0) = \frac{2\mu_0}{3k_B T}, \quad \chi_\sigma(T, J=0) = 0$$

The physical interpretation of these results is as follows. When  $J = 0$ , the individual dimer Hamiltonian is  $\hat{h} = -\mu_0 H S$ . The factor of  $\frac{2}{3}$  in  $\chi_S$  is due to the fact that  $S = 0$  in  $\frac{1}{3}$  of the states. The  $\sigma$  spins don't couple to the field at all in this limit, so  $\chi_\sigma = 0$ .

(2) Recall that a van der Waals gas obeys the equation of state

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT,$$

where  $v$  is the molar volume. We showed that the energy per mole of such a gas is given by

$$\varepsilon(T, v) = \frac{1}{2} f RT - \frac{a}{v},$$

where  $T$  is temperature and  $f$  is the number of degrees of freedom per particle.



(a) For an ideal gas, the adiabatic equation of state is  $vT^{f/2} = \text{const}$ . Find the adiabatic equation of state (at fixed particle number) for the van der Waals gas.

(b) One mole of a van der Waals gas is used as the working substance in a Carnot engine (see Fig. 1). Find the molar volume at  $v_C$  in terms of  $v_B, T_1, T_2$ , and constants.

(c) Find the heat  $Q_{AB}$  absorbed by the gas from the upper reservoir.

(d) Find the work done per cycle,  $W_{\text{cyc}}$ . *Hint: you only need to know  $Q_{AB}$  and the cycle efficiency  $\eta$ .*

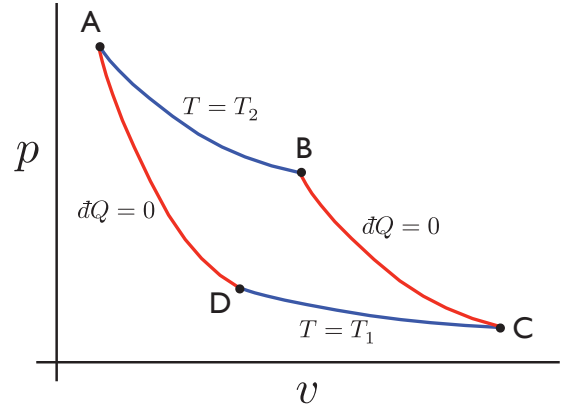


Figure 1: The Carnot cycle.

**Solution :**

(a) We have

$$\begin{aligned} 0 &= T ds = d\varepsilon + p dv \\ &= \frac{1}{2}fR dT + \left(p + \frac{a}{v^2}\right) dv \\ &= \frac{1}{2}fR dT + \frac{RT dv}{v-b} = \frac{1}{2}fRT d\ln[(v-b)T^{f/2}] , \end{aligned}$$

where  $s = N_A S/N$  is the molar entropy. Thus, the adiabatic equation of state for the van der Waals gas is

$$ds = 0 \Rightarrow (v-b)T^{f/2} = \text{const.}$$

Setting  $b = 0$ , we recover the ideal gas result.

(b) Since BC is an adiabat, we have

$$(v_B - b)T_2^{f/2} = (v_C - b)T_1^{f/2} \Rightarrow v_C = b + (v_B - b) \left(\frac{T_2}{T_1}\right)^{f/2}$$

(c) We have, from the First Law,

$$\begin{aligned} Q_{AB} &= E_B - E_A + W_{AB} \\ &= \nu \left(\frac{a}{v_A} - \frac{a}{v_B}\right) + \nu \int_{v_A}^{v_B} dv p \\ &= \nu \left(\frac{a}{v_A} - \frac{a}{v_B}\right) + \nu \int_{v_A}^{v_B} dv \left[\frac{RT_2}{v-b} - \frac{a}{v^2}\right] , \end{aligned}$$

hence

$$Q_{AB} = \nu R T_2 \ln \left( \frac{v_B - b}{v_A - b} \right)$$

with  $\nu = 1$ .

(d) Since the cycle is reversible, we must have

$$\eta = \frac{W_{\text{cyc}}}{Q_{AB}} \Rightarrow W_{\text{cyc}} = \nu R (T_2 - T_1) \ln \left( \frac{v_B - b}{v_A - b} \right)$$

(3) In homework assignment #9, you showed that the grand partition function for a gas of  $q$ -state parafermions is

$$\Xi(T, V, \mu) = \prod_{\alpha} \left( \frac{1 - e^{(q+1)(\mu - \varepsilon_{\alpha})/k_B T}}{1 - e^{(\mu - \varepsilon_{\alpha})/k_B T}} \right),$$

where the product is over all single particle states. Consider now the case where the number of parafermions is not conserved, hence  $\mu = 0$ . We call such particles *paraphotons*.

(a) What is the occupancy  $n(\varepsilon, T)$  of  $q$ -state paraphotons of energy  $\varepsilon$ ?

(b) Suppose the dispersion is the usual  $\varepsilon(\mathbf{k}) = \hbar c k$ . Assuming  $g = 1$ , find the single particle density of states  $g(\varepsilon)$  in three space dimensions.

(c) Find the pressure  $p(T)$ . You may find the following useful:

$$\int_0^{\infty} dt \frac{t^{r-1}}{e^t - 1} = \Gamma(r) \zeta(r) \quad , \quad \int_0^{\infty} dt t^{r-1} \ln \left( \frac{1}{1 - e^{-t}} \right) = \Gamma(r) \zeta(r + 1).$$

(d) Show that  $p = C_q n k_B T$ , where  $n$  is the number density, and  $C_q$  is a dimensionless constant which depends only on  $q$ .

**Solution :**

(a) For  $\mu \neq 0$ , for a single parafermion state, we have

$$\begin{aligned} n &= -\frac{\partial \Omega}{\partial \mu} = \frac{1}{\beta} \frac{\partial \ln \Xi}{\partial \mu} \\ &= \frac{1}{e^{\beta(\varepsilon - \mu)} - 1} - \frac{q + 1}{e^{(q+1)\beta(\varepsilon - \mu)} - 1}. \end{aligned}$$

Setting  $\mu = 0$ , we find

$$n(\varepsilon, T) = \frac{1}{e^{\varepsilon/k_B T} - 1} - \frac{q + 1}{e^{(q+1)\varepsilon/k_B T} - 1}$$

(b) With  $g = 1$ , we have

$$g(\varepsilon) d\varepsilon = \frac{d^3k}{(2\pi)^3} = \frac{k^2 dk}{2\pi^2} \Rightarrow \boxed{g(\varepsilon) = \frac{k^2}{2\pi^2} \frac{dk}{d\varepsilon} = \frac{\varepsilon^2}{2\pi^2(\hbar c)^3}}$$

(c) The pressure is

$$\begin{aligned} p &= -\frac{\Omega}{V} = k_B T \int_0^\infty d\varepsilon g(\varepsilon) \left\{ \ln(1 - e^{-(q+1)\varepsilon/k_B T}) - \ln(1 - e^{-\varepsilon/k_B T}) \right\} \\ &= \frac{k_B T}{2\pi^2(\hbar c)^3} \int_0^\infty d\varepsilon \varepsilon^2 \left\{ \ln(1 - e^{-(q+1)\varepsilon/k_B T}) - \ln(1 - e^{-\varepsilon/k_B T}) \right\} \\ &= \frac{\zeta(4) (k_B T)^4}{\pi^2(\hbar c)^3} \cdot \left( 1 - \frac{1}{(q+1)^3} \right). \end{aligned}$$

Thus,

$$\boxed{p(T) = \left( 1 - (q+1)^{-3} \right) \cdot \frac{\zeta(4) (k_B T)^4}{\pi^2(\hbar c)^3}}$$

(d) We need to evaluate

$$\begin{aligned} n &= \int_0^\infty d\varepsilon g(\varepsilon) \left\{ \frac{1}{e^{\varepsilon/k_B T} - 1} - \frac{q+1}{e^{(q+1)\varepsilon/k_B T} - 1} \right\} \\ &= \frac{1}{2\pi^2(\hbar c)^3} \int_0^\infty d\varepsilon \varepsilon^2 \left\{ \frac{1}{e^{\varepsilon/k_B T} - 1} - \frac{q+1}{e^{(q+1)\varepsilon/k_B T} - 1} \right\} \\ &= \left( 1 - (q+1)^{-2} \right) \cdot \frac{\zeta(3) (k_B T)^3}{\pi^2(\hbar c)^3} \end{aligned}$$

From this we derive

$$\boxed{C_q = \frac{p}{nk_B T} = \frac{\zeta(4)}{\zeta(3)} \cdot \frac{q^2 + 3q + 3}{q^2 + 3q + 2}}$$

**(4)** Provide brief but substantial answers to the following:

(a) A particle in  $d = 3$  dimensions has the dispersion  $\varepsilon(\mathbf{k}) = \varepsilon_0 \exp(ka)$ . Find the density of states per unit volume  $g(\varepsilon)$ . Sketch your result.

(b) Find the information entropy in the distribution  $p_n = C e^{-\lambda n}$ , where  $n \in \{0, 1, 2, \dots\}$ . Choose  $C$  so as to normalize the distribution.

(c) An ideal gas at temperature  $T = 300$  K undergoes an adiabatic free expansion which results in a doubling of its volume. What is the final temperature?

(d) For an  $N$ -particle noninteracting system, sketch the contributions  $\Delta C_V$  to the heat capacity *versus* temperature for (i) a vibrational mode at energy  $\hbar\omega_0$ , and (ii) a two-level (Schottky) defect with energy splitting  $\Delta = \varepsilon_1 - \varepsilon_0$ . Take care to identify any relevant characteristic temperatures, as well as the limiting values of  $\Delta C_V$ .

**Solution :**

(a) Inverting the dispersion relation, we obtain the expression  $k(\varepsilon) = a^{-1} \ln(\varepsilon/\varepsilon_0) \Theta(\varepsilon - \varepsilon_0)$ . We then have

$$g(\varepsilon) = \frac{k^2}{2\pi} \frac{dk}{d\varepsilon} = \frac{k^2}{2\pi} \cdot \frac{1}{a\varepsilon_0 e^{ak}}.$$

Thus,

$$g(\varepsilon) = \frac{1}{2\pi^2 a^3} \frac{1}{\varepsilon} \ln^2\left(\frac{\varepsilon}{\varepsilon_0}\right) \Theta(\varepsilon - \varepsilon_0)$$

The result is plotted in Fig. 2.

(b) Normalizing the distribution,

$$1 = \sum_{n=0}^{\infty} p_n = C \sum_{n=0}^{\infty} e^{-n\lambda} = \frac{C}{1 - e^{-\lambda}},$$

hence  $C = 1 - e^{-\lambda}$ . The information entropy is

$$S = - \sum_{n=0}^{\infty} p_n \ln p_n = - \ln(1 - e^{-\lambda}) + C\lambda \sum_{n=0}^{\infty} n e^{-\lambda n}.$$

Now

$$f(\lambda) = \sum_{n=0}^{\infty} e^{-n\lambda} = \frac{1}{1 - e^{-\lambda}} \Rightarrow \sum_{n=0}^{\infty} n e^{-n\lambda} = -\frac{df}{d\lambda} = \frac{1}{(e^\lambda - 1)(1 - e^{-\lambda})}.$$

Thus, the information entropy is

$$S(\lambda) = \frac{\lambda}{e^\lambda - 1} - \ln(1 - e^{-\lambda}).$$

Note that  $S(\lambda \rightarrow 0) \sim 1 - \ln \lambda$  which diverges logarithmically with  $1/\lambda$ . This is approaching the uniform distribution. For  $\lambda \rightarrow \infty$ , we have  $p_n = \delta_{n,0}$ , and  $S(\lambda \rightarrow \infty) = 0$ .

(c) Under an adiabatic free expansion,  $\Delta E = Q = W = 0$  with  $N$  conserved. Since  $E = \frac{1}{2} f N k_B T$  is independent of volume for the ideal gas, there is no change in temperature, *i.e.*

$$T_{\text{final}} = T_{\text{initial}} = 100 \text{ K}$$

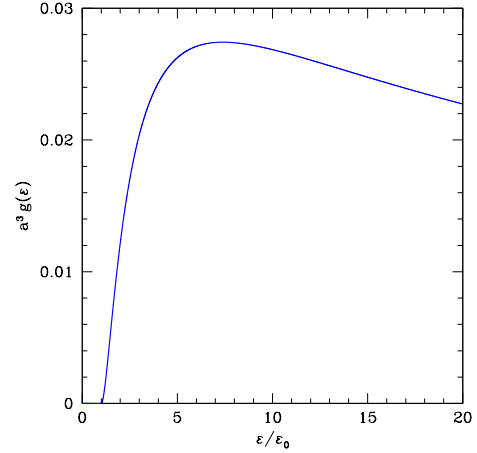


Figure 2: DOS for problem 4.a.

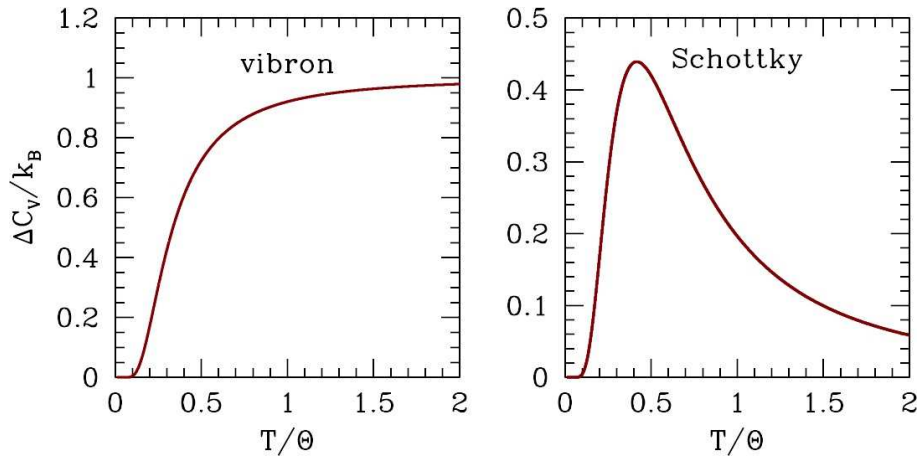


Figure 3: Heat capacities for a  $N$  identical vibrational modes (left) and Schottky defects (right).

(d) The characteristic temperatures for the vibrational mode (vibron) and Schottky defect are given by  $\theta = \hbar\omega_0/k_B$  and  $\theta = \Delta/k_B$ , respectively. A detailed derivation of the heat capacity for these systems is provided in §§ 4.10.5-6 of the Lecture Notes. One finds

$$\Delta C_V = Nk_B \left( \frac{\theta}{T} \right)^2 \frac{e^{\theta/T}}{(e^{\theta/T} \mp 1)^2},$$

where the top sign is for the vibron and the bottom sign for the Schottky defect. All you were asked to do, however, was to provide a sketch (see Fig. 3). The  $T \rightarrow \infty$  limit of the vibron result is given by the Dulong-Petit value of  $k_B$  per oscillator mode. For the Schottky defect,  $\Delta C_V$  vanishes in both the  $T \rightarrow 0$  and  $T \rightarrow \infty$  limits.

(5) Write a well-defined expression for the greatest possible number expressible using only five symbols. Examples:  $1 + 2 + 3$ ,  $10^{100}$ ,  $\Gamma(99)$ . [50 quatlous extra credit]

**Solution :**

Using conventional notation, my best shot would be

$$9^{9^{9^9}}$$

This is a very big number indeed:  $9^9 \approx 3.7 \times 10^8$ , so  $9^{9^9} \sim 10^{3.7 \times 10^8}$ , and  $9^{9^{9^9}} \sim 10^{10^{3.7 \times 10^8}}$ . But in the world of big numbers, this is still tiny. For a fun diversion, use teh google to learn about the Ackermann sequence and Knuth's up-arrow notation. Using Knuth's notation (see [http://en.wikipedia.org/wiki/Knuth's\\_up-arrow\\_notation](http://en.wikipedia.org/wiki/Knuth's_up-arrow_notation)), one could write  $9 \uparrow^{99} 9$ , which is vastly larger. But even *these* numbers are modest compared with something called the "Busy Beaver sequence", which is a concept from computer science and Turing machines. For a very engaging essay on large numbers, see <http://www.scottaaronson.com/writings/bignumbers.html>.