PHYS 328

SECOND HOUR EXAM-- FALL 2013

Solutions

1. a) The entropy of the system will be determined by the multiplicity of states according to :

$$S = k \ln \Omega$$

and we can find Ω by computing the number of ways we can choose N_R steps out of a total of N steps:

$$\Omega = \frac{N!}{N_R!\,(N - N_R)!}$$

Using Stirling's approximation we can write :

$$S = k \ln \Omega = k[\ln N! - \ln N_R! - \ln (N - N_R)!] =$$
$$k[N \ln N - N - (N_R \ln N_R - N_R) - (N - N_R) \ln (N - N_R) - (N - N_R)]$$
$$= k[N \ln N - N_R \ln N_R - (N - N_R) \ln (N - N_R)]$$

b) The total displacement L must be equal to the excess of links to the right over links to the left times the length of each step, so we have :

$$L = (N_R - N_L)\, d = (N_R - (N - N_R))\, d = (2 N_R - N)\, d$$

where we make use of the fact that the number of links to the left and right must sum to the total number of links N.

c) The thermodynamic identity is :

$$dU = T\, dS - P\, dV + \mu\, dN$$

If dN is zero and L replaces V and F replaces P we have :

$$dU = T\, dS + F\, dL$$

the positive sign making sense since pulling the band represents the work done on the system which is positive.

d) The partition function is the sum of Boltzmann factors. Since there are only two allowable states (left and right) there are only two terms in the partition function :

$$Z = \sum_s e^{-\beta E_s} = e^{-\beta(-\epsilon)} + e^{-\beta \epsilon} = e^{\beta \epsilon} + e^{-\beta \epsilon} = 2 \cosh (\beta \epsilon)$$

e) Since the particles are indistinguishable, we use the form of the N - particle partition function :

$$Z^N = \frac{1}{N!} Z_1^N = \frac{1}{N!} (2 \cosh (\beta \epsilon))^N$$

Then, we find the Helmholtz Free Energy from :

$$F = -kT\ln Z = -kT\ln\left[(2\cosh(\beta\epsilon))^N / N!\right]$$

you could expand the log but it is fine if you did not.

f) We can use the relationship:

$$\overline{U} = \frac{-1}{Z}\frac{\partial Z}{\partial\beta} = -\frac{\partial \ln Z}{\partial\beta}$$

we know from part d) that ln Z = ln (2 cosh ($\beta\,\epsilon$)) so that

$$U = \frac{-1}{2\cosh(\beta\epsilon)}\cdot 2\epsilon\sinh(\beta\epsilon) = -\epsilon\tanh(\beta\epsilon)$$

(which is the same result as for the average energy of a paramagnet solved on p. 104 in Ch. 3 and on p. 232 in Ch. 6)

g) Extra credit : Follow the logic used on p. 110 of the text to show that :

$$P = T\left(\frac{\partial S}{\partial V}\right)_{U,N}$$

If here we are replacing V with L and P with - F, we have :

$$F = -T\left(\frac{\partial S}{\partial L}\right)_U$$

Dimensionally we have units of force on the left; the units of entropy are J/K and the units of length are m, so on the right we have units of (J/K/m)·K = J/m. You know from the simple definition of work that W = force x length so that F has units of work/distance, so the equation is dimensionally consistent.

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2. a) We begin with :

$$dU = T\,dS - P\,dV + \mu\,dN$$

$$G = U - TS + PV \Rightarrow dG = dU - T\,dS + S\,dT + P\,dV + V\,dP$$

$$F = U - TS \Rightarrow dF = dU - T\,dS - S\,dT$$

Substituting the thermodynamic identity in dU in the expressions for dG and dF yields :

$$dG = -S\,dT + V\,dP + \mu\,dN$$

$$dF = -S\,dT - P\,dV + \mu\,dN$$

b) Taking partials :

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

c) Taking partials :

$$\left(\frac{\partial G}{\partial T}\right)_{P,N} = -S \quad \left(\frac{\partial G}{\partial P}\right)_{T,N} = V \quad \left(\frac{\partial G}{\partial N}\right)_{T,P} = \mu$$

d) If we look at the last relationship in part c), and do the partial integration, we get :

$$G = \mu N + G_0$$

Dividing through by N allows us to see that chemical potential is simply G/particle.

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3. a) The probability of finding the oscillator in the 3 ϵ state compared to the 0 energy state is the ratio of Boltzmann factors :

$$\frac{P(3\epsilon)}{P(0)} = \frac{e^{-3\beta\epsilon}}{e^{-0}} = e^{-3\beta\epsilon}$$

b) If there are many states available to the oscillator, the partition function is the sum over many terms of :

$$Z = \sum_n e^{-\beta E(n)} = e^{-0} + e^{-1\beta\epsilon} + e^{-2\beta\epsilon} + e^{-3\beta\epsilon} + \ldots e^{-n\beta\epsilon} =$$

$$1 + e^{-\beta\epsilon} + \left(e^{-\beta\epsilon}\right)^2 + \left(e^{-\beta\epsilon}\right)^3 + \ldots \left(e^{-\beta\epsilon}\right)^n = \sum_0^\infty e^{-n\beta\epsilon} = \sum_{n=0}^\infty \left(e^{-\beta\epsilon}\right)^n$$

Now, if we set x = $e^{-\beta\epsilon}$ we have a sum of the form $\sum_{n=0}^\infty x^n$ and we can write:

$$Z = \frac{1}{1-x} = \frac{1}{1-e^{-\beta\epsilon}}$$

c) Extra credit :

Using the expression :

$$\overline{E} = \frac{-1}{Z}\frac{\partial Z}{\partial \beta}$$

$$\frac{\partial Z}{\partial \beta} = \frac{-1}{\left(1-e^{-\beta\epsilon}\right)^2} \cdot \epsilon\, e^{-\beta\epsilon}$$

so that dividing this by Z gives :

$$\overline{E} = -\left(1-e^{-\beta\epsilon}\right) \cdot \frac{-1}{\left(1-e^{-\beta\epsilon}\right)^2} \cdot \epsilon\, e^{-\beta\epsilon} = \frac{\epsilon\, e^{-\beta\epsilon}}{1-e^{-\beta\epsilon}}$$

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4. The average of any distribution can be written as :

$$\overline{x} = \sum_s x(s)\, P(s) = \sum_s x(s)\, N \frac{(s)}{N} = \frac{1}{\mathcal{Z}} \sum_s x(s)\, e^{-(\epsilon(s) - \mu N(s))/kT}$$

So that the average number of of particles in a system is :

$$\overline{N} = \frac{1}{\mathcal{Z}} \sum_s N(s)\, e^{-(\epsilon(s) - \mu N(s))/kT}$$

Let' s differentiate the grand partition function with respect to μ as the identity suggests :

$$\frac{\partial \mathcal{Z}}{\partial \mu} = \Sigma \frac{N(s)}{kT} e^{-(\epsilon(s) - \mu N(s))/kT}$$

If we multiply this expression by $kT/\mathcal{Z}$, we show that :

$$\overline{N} = \frac{kT}{\mathcal{Z}} \frac{\partial \mathcal{Z}}{\partial \mu}$$