1. (50 points) Say you have a stretched plastic rod with tension force

$$F = aT^2(L - L_0)$$

where L is the stretched length, the constant L_0 is the unstretched length, and a is an overall proportionality constant. When $L = L_0$, the rod's heat capacity at constant length is $C_L = bT$, where b is a constant.

(a) Write down the fundamental thermodynamic relation for this system, expressing dS in terms of dU and dL. (*Hint:* You've done something very similar in one of your homework problems.)

Answer: As in problem 3.34, $dU = TdS + FdL$.

(b) The entropy $S(T, L)$ is a function of T and L. Calculate $(\partial S/\partial L)_T$. (*Hint:* Use a Maxwell relationship you can derive for the rod.)

Answer: The Maxwell relation we need involves the mixed partial derivatives of the Helmholtz free energy, with $d\mathcal{F} = FdL - SdT$. Therefore,

$$\left(\frac{\partial \mathcal{F}}{\partial L}\right)_T = F \qquad \text{and} \qquad \left(\frac{\partial \mathcal{F}}{\partial T}\right)_L = -S$$

And now, since

$$\frac{\partial^2 \mathcal{F}}{\partial L \partial T} = \frac{\partial^2 \mathcal{F}}{\partial T \partial L} \quad \Rightarrow \quad \left(\frac{\partial F}{\partial T}\right)_L = -\left(\frac{\partial S}{\partial L}\right)_T$$

This means that

$$\left(\frac{\partial S}{\partial L}\right)_T = -\left(\frac{\partial F}{\partial T}\right)_L = -2aT(L - L_0)$$

(c) Say you know $S(T_0, L_0)$ for some temperature T_0. Find $S(T, L_0)$.

Answer: First, observe that $C_L = (\partial U/\partial T)_L = T(\partial S/\partial T)_L$. Then, with $S(T, L)$,

$$\begin{aligned} dS &= \left(\frac{\partial S}{\partial T}\right)_L dT + \left(\frac{\partial S}{\partial L}\right)_T dL = \frac{C_L}{T}\, dT - \left(\frac{\partial F}{\partial T}\right)_L dL \\ &= b\, dT - 2aT(L - L_0)\, dL \end{aligned}$$

Looking for $S(T, L_0)$ means holding L constant, so $dL = 0$. Therefore

$$S(T, L_0) = S(T_0, L_0) + \int_{T_0}^{T} dT \, \frac{C_L}{T} = S(T_0, L_0) + b(T - T_0)$$

(d) Now find $S(T, L)$, the entropy at any temperature and length.

Answer: Now, we can begin with the already found $S(T, L_0)$, hold T constant, and integrate over L:

$$\begin{aligned} S(T, L) &= S(T, L_0) - 2aT \int_{L_0}^{L} dL \, (L - L_0) \\ &= S(T_0, L_0) + b(T - T_0) - aT \, (L - L_0)^2 \end{aligned}$$

2. (50 points) Say you have a system where the energy levels are labeled by $n = 1, 2, 3, \ldots$, and where the energy of each level is $E_n = n\epsilon$, where ϵ is a constant. Each energy level n is n-fold degenerate, so that there are 2 states with E_2, 3 states with E_3, and so on. This system is in contact with a temperature reservoir at temperature T.

(a) Find an exact value for the partition function as a function of T. (*Hint:* Use the same trick I did in class to relate $\bar{E}$ to a derivative of Z, which also gives the answer to problem 6.16. Any infinite series you actually sum should be one that you recognize from one of your other homework problems.)

Answer: Summing the Boltzmann factors,

$$Z = \sum_n n \, e^{-\beta n \epsilon} = -\frac{1}{\epsilon} \frac{\partial}{\partial \beta} \sum_n e^{-\beta n \epsilon} = -\frac{1}{\epsilon} \frac{\partial}{\partial \beta} \frac{1}{1 - e^{-\beta \epsilon}} = \frac{e^{-\beta \epsilon}}{(1 - e^{-\beta \epsilon})^2}$$

(b) Find $\bar{E}$ for this system. Check your result in the $kT \gg \epsilon$ and $kT \ll \epsilon$ limits, and explain whether these limits make sense.

Answer: As usual,

$$\bar{E} = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = \epsilon\left[1 + \frac{2\,e^{-\beta\epsilon}}{1 - e^{-\beta\epsilon}}\right]$$

When $kT \gg \epsilon$, $\bar{E} \to \epsilon$. This is what we should expect; at $T \to 0$ the particle will have to occupy the lowest energy state with $n = 1$ and $E_1 = \epsilon$, and $p_n = 0$ for $n > 1$.

When $kT \ll \epsilon$, $(1 - e^{-\beta\epsilon}) \to \beta\epsilon$. Therefore

$$\bar{E} \to \epsilon\left[1 + \frac{2kT}{\epsilon}\right] \to 2kT$$

You are used to seeing $\bar{E} = f(\frac{1}{2}kT)$ at large kT due to equipartition; this fits the pattern.

(c) You distribute N noninteracting, distinguishable particles among these energy levels. Find the entropy $S(T, N)$. (*Hint:* You did a homework problem that was very similar.)

Answer: Use the Helmholtz free energy:

$$F = -kT\ln Z = \epsilon + 2kT\ln(1 - e^{-\epsilon/kT})$$

Now, multiply that with N (for N particles) and use

$$\begin{aligned} S &= -\left(\frac{\partial F}{\partial T}\right)_N = -2kN\ln(1 - e^{-\epsilon/kT}) + 2kNT\frac{e^{-\epsilon/kT}}{1 - e^{-\epsilon/kT}}\frac{\epsilon}{kT^2} \\ &= 2kN\left[\frac{e^{-\epsilon/kT}}{1 - e^{-\epsilon/kT}}\frac{\epsilon}{kT} - \ln(1 - e^{-\epsilon/kT})\right] \end{aligned}$$