1. (40 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. (60 points) Look at a *three*-state paramagnet. In this model, together with spin up and spin down, which have energies $\pm\mu B$ when in an external magnetic field, each spin also can be in a spin 0 state where the energy is 0. There are N of these spins, which do not interact with each other. N is a very large number.

(a) Find the energy $U(T)$ of this system, as a function of temperature.

Answer: The single-particle partition function is

$$Z_1 = e^{\beta\mu B} + 1 + e^{-\beta\mu B} = 1 + 2\cosh\beta\mu B$$

Then,

$$\bar{E} = -\frac{1}{Z_1}\frac{\partial Z_1}{\partial \beta} = -\frac{2\mu B \sinh\beta\mu B}{1 + 2\cosh\beta\mu B}$$

For N particles, to an excellent approximation,

$$U = N\bar{E} = -\frac{2N\mu B \sinh\beta\mu B}{1 + 2\cosh\beta\mu B}$$

(b) Find the entropy $S(T)$ of this system, as a function of temperature.

Answer: The N-particle partition function is $Z = Z_1^N$. Therefore

$$\mathcal{F} = -kT \ln Z = -NkT \ln\left[1 + 2\cosh(\mu B/kT)\right]$$

$$\begin{aligned} S &= -\left(\frac{\partial \mathcal{F}}{\partial T}\right)_{V,N} \\ &= Nk \ln\left[1 + 2\cosh(\mu B/kT)\right] - \frac{N\mu B}{T}\left[\frac{2\sinh(\mu B/kT)}{1 + 2\cosh(\mu B/kT)}\right] \end{aligned}$$

(c) Find U and S for $T = 0$ and $T = \infty$. Interpret your results in terms of the spin configurations of the paramagnet and the multiplicity Ω at these temperature limits. *Note:* $T = 0^+$ and $T = 0^-$ are different!

Answer: At $T \to 0$, $2\cosh(\mu B/kT) \to e^{\mu B/kT}$ and $2\sinh(\mu B/kT) \to e^{\mu B/kT}$. Therefore,

$$S(T = 0) = Nk \ln e^{\mu B/kT} - \frac{N\mu B}{T} = 0$$

The energy depends on whether you approach $T = 0$ from then positive or negative direction, since the sinh factor will flip its sign

$$U(T = 0^\pm) = \mp N\mu B$$

This is exactly what you expect at $T = 0$ for a nondegenerate ground state. As $T \to 0^+$, the minimum energy state will be that with all spins aligned with the external magnetic field. At the extreme hot limit, as $T \to 0^-$, the minimum energy state will be that with all spins aligned against the external magnetic field. In both cases, the multiplicity Ω is 1, and therefore $S = k \ln \Omega = 0$.

As $T \to \infty$, $2\cosh(\mu B/kT) \to 2$ and $2\sinh(\mu B/kT) \to 0$. Therefore,

$$S(T = \infty) = Nk \ln 3 \qquad U(T = \infty) = 0$$

The numbers of spin up, down, and 0 states will be equal to $N/3$, so for large N, the entropy goes like

$$S/k = \ln \Omega = \ln \frac{N!}{\left(\frac{N}{3}\right)!^3} = N \ln N - N - 3\left(\tfrac{N}{3} \ln \tfrac{N}{3} - \tfrac{N}{3}\right) = N \ln 3$$

Therefore, the entropy and energy are as they should be.

(d) Define $t = \mu B/kT$, and make a plot of $S(t)/Nk$ for t from -8 to $+8$.

Answer: Plotting

$$\frac{S(t)}{Nk} = \ln\left(1 + 2\cosh t\right) - t\left(\frac{2\sinh t}{1 + 2\cosh t}\right)$$

we get