
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,

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

And now, since

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

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

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

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

(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 $T \rightarrow 0$, $2 \cosh(\mu B/kT) \rightarrow e^{\mu B/kT}$ and $2 \sinh(\mu B/kT) \rightarrow e^{\mu B/kT}$. 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 the 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 $T \rightarrow 0^+$, the minimum energy state will be that with all spins aligned with the external magnetic field. At the extreme hot limit, as $T \rightarrow 0^-$, 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 $T \rightarrow \infty$, $2 \cosh(\mu B/kT) \rightarrow 2$ and $2 \sinh(\mu B/kT) \rightarrow 0$. Therefore,

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

The numbers of spin up, down, and 0 states will be equal, so the multiplicity is $\Omega = 3^N$, hence 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

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

we get

