

Problem 3.33. In an constant-volume process, the thermodynamic identity reduces to $dU = T dS$. Making this substitution for dU in the definition of C_V gives

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = T \left(\frac{\partial S}{\partial T} \right)_V.$$

To derive a similar formula for C_P , we need a “thermodynamic identity” for the enthalpy H . From its definition $H = U + PV$, we have

$$dH = dU + d(PV) = dU + P dV + V dP = T dS + V dP,$$

where the last step follows from the ordinary thermodynamic identity. In a constant-pressure process, therefore, $dH = T dS$, so

$$C_P = \left(\frac{\partial H}{\partial T} \right)_P = T \left(\frac{\partial S}{\partial T} \right)_P.$$

Problem 3.34. (Rubber band model.)

- (a) Each link can point either left or right, so this system is mathematically the same as a collection of coins or a two-state paramagnet. The multiplicity is $\Omega = \binom{N}{N_R}$, so the entropy is

$$\begin{aligned} \frac{S}{k} &= \ln \Omega = k \ln \binom{N}{N_R} = \ln \left(\frac{N!}{N_R! (N - N_R)!} \right) \\ &\approx N \ln N - N - (N_R \ln N_R - N_R) - [(N - N_R) \ln(N - N_R) - (N - N_R)] \\ &= N \ln N - N_R \ln N_R - (N - N_R) \ln(N - N_R), \end{aligned}$$

in analogy with equation 3.28.

- (b) Each right-pointing link increases L by ℓ , while each left-pointing link decreases L by ℓ , so the net length must be

$$L = \ell(N_R - N_L) = \ell(2N_R - N), \quad \text{or} \quad N_R = \frac{1}{2} \left(\frac{L}{\ell} + N \right).$$

- (c) If L is analogous to V and F is analogous to $-P$, then the thermodynamic identity should be

$$dU = T dS + F dL.$$

The second term makes sense: It is the work (force times displacement) done on the system by quasistatically stretching it an amount dL .

- (d) Imagine a process for which $dU = 0$. Then the thermodynamic identity says that $F dL = -T dS$, or

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

For our system, it is convenient to express this partial derivative in terms of N_R , using the chain rule:

$$\frac{\partial S}{\partial L} = \frac{\partial S}{\partial N_R} \frac{\partial N_R}{\partial L} = \frac{\partial S}{\partial N_R} \frac{1}{2\ell}.$$

Therefore, by the result of part (a),

$$F = -\frac{kT}{2\ell} \left[-\ln N_R - \frac{N_R}{N_R} + \ln(N - N_R) + \frac{N - N_R}{N - N_R} \right] = -\frac{kT}{2\ell} \ln \left(\frac{N - N_R}{N_R} \right).$$

The result of part (b) can be used to write this in terms of L :

$$F = -\frac{kT}{2\ell} \ln \left(\frac{2}{L/N\ell + 1} - 1 \right) = -\frac{kT}{2\ell} \ln \left(\frac{1 - L/N\ell}{1 + L/N\ell} \right) = \frac{kT}{2\ell} \ln \left(\frac{1 + L/N\ell}{1 - L/N\ell} \right).$$

(e) When $L \ll N\ell$, the argument of the logarithm is approximately

$$\frac{1 + L/N\ell}{1 - L/N\ell} \approx (1 + L/N\ell)(1 + L/N\ell) \approx 1 + \frac{2L}{N\ell},$$

so the logarithm itself is approximately $2L/N\ell$ and therefore

$$F \approx \frac{kT}{2\ell} \frac{2L}{N\ell} = \frac{kTL}{N\ell^2}.$$

This expression is linear in L ; it has the form of Hooke's law, with the "spring constant" equal to $kT/N\ell^2$.

- (f) The tension is proportional to T , so it's greater at high temperature than at low temperature. For a given tension, increasing T should cause the rubber band to contract: L must decrease to compensate. Although this behavior is opposite to that of an ideal gas, it *does* make sense if you think about it. At higher temperature there should be more randomness in the orientation of the links, causing the rubber band to contract.
- (g) Under such an adiabatic stretching, the total entropy of the rubber band should be constant. Since stretching the rubber band decreases the configurational entropy computed in part (a), the vibrational entropy must increase to compensate. But this implies an increase in the number of units of vibrational energy, and therefore an increase in temperature. I tested this prediction with a real rubber band as suggested, and the effect is subtle but noticeable.

Problem 3.35. With three oscillators and four units of energy, the multiplicity is $\binom{4+3-1}{4} = 15$. If we now add an oscillator without removing any energy, the multiplicity increases to $\binom{4+4-1}{4} = 35$. If we remove one unit of energy, the multiplicity is then $\binom{3+4-1}{3} = 20$, still larger than what we started with. If we remove two units of energy, the multiplicity decreases to $\binom{2+4-1}{2} = 10$, which is too small. So apparently, to hold the multiplicity (and entropy) fixed while adding an oscillator, we need to remove somewhere between one and two units of energy (whatever that means), i.e., μ is somewhere between $-\epsilon$ and -2ϵ .