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

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

(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, usin 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

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

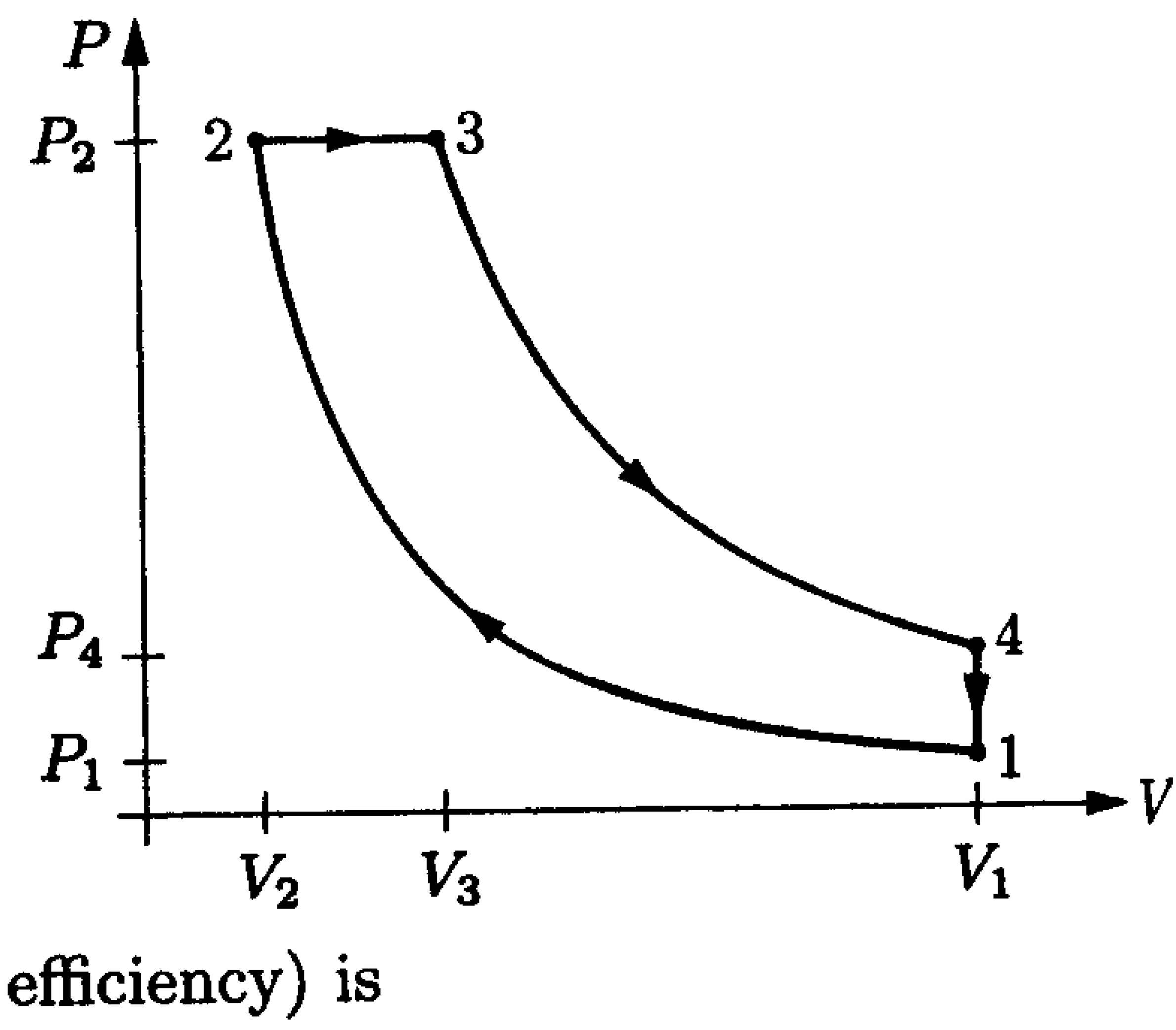
This expression is linear in L; it has the form of Hooke's law, with the "spring constan equal to $kT/N\ell^2$.

(f) The tension is proportional to T, so it's greater at high temperature than at l temperature. For a given tension, increasing T should cause the rubber band contract: L must decrease to compensate. Although this behavior is opposite to th of an ideal gas, it *does* make sense if you think about it. At higher temperature the should be more randomness in the orientation of the links, causing the rubber ba to contract.

(g) Under such an adiabatic stretching, the total entropy of the rubber band should constant. Since stretching the rubber band decreases the configurational entropy co puted in part (a), the vibrational entropy must increase to compensate. But this i plies an increase in the number of units of vibrational energy, and therefore an increa in temperature. I tested this prediction with a real rubber band as suggested, and t 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 increa to $\binom{4+4-1}{4} = 35$. If we remove one unit of energy, the multiplicity is then $\binom{3+4-1}{3} =$ still larger than what we started with. If we remove two units of energy, the multiplic decreases to $\binom{2+4-1}{2} = 10$, which is too small. So apparently, to hold the multiplicity (a entropy) fixed while adding an oscillator, we need to remove somewhere between one a two units of energy (whatever that means), i.e., μ is somewhere between $-\epsilon$ and -2ϵ.

Problem 4.20. Following the same method as in Problem 4.18, the heat input (during step 2–3) is



$$Q_h = (U_3 - U_2) + P_2(V_3 - V_2)$$
$$= \frac{f}{2}Nk(T_3 - T_2) + P_2(V_3 - V_2)$$
$$= \frac{f+2}{2}P_2(V_3 - V_2),$$

while the waste heat output is

$$Q_c = U_4 - U_1 = \frac{f}{2}V_1(P_4 - P_1).$$

Therefore the ratio of heats (which is 1 minus the efficiency) is

$$\frac{Q_c}{Q_h} = \frac{\frac{f}{2}\cdot V_1(P_4 - P_1)}{\frac{f+2}{2}\cdot P_2(V_3 - V_2)} = \frac{1}{\gamma}\frac{V_1(P_4 - P_1)}{P_2(V_3 - V_2)}.$$

Since steps 3–4 and 1–2 are adiabatic, we can relate the initial and final pressures:

$$P_4V_1^\gamma = P_2V_3^\gamma; \qquad P_1V_1^\gamma = P_2V_2^\gamma.$$

Solving these equations for P_4 and P_1, respectively, and plugging into the previous equation gives

$$\frac{Q_c}{Q_h} = \frac{1}{\gamma}\frac{V_1}{V_3 - V_2}\left[\left(\frac{V_3}{V_1}\right)^\gamma - \left(\frac{V_2}{V_1}\right)^\gamma\right].$$

To better understand this result, divide the numerator and denominator of each volume ratio by V_2, then factor out the compression ratio to obtain

$$\frac{Q_c}{Q_h} = \frac{1}{\gamma}\frac{V_1/V_2}{(V_3/V_2) - 1}\left[\left(\frac{V_3}{V_2}\right)^\gamma\left(\frac{V_2}{V_1}\right)^\gamma - \left(\frac{V_2}{V_1}\right)^\gamma\right] = \left(\frac{V_2}{V_1}\right)^{\gamma-1}\cdot\frac{1}{\gamma}\frac{(V_3/V_2)^\gamma - 1}{(V_3/V_2) - 1}.$$

The efficiency is just 1 minus this quantity,

$$e = 1 - \left(\frac{V_2}{V_1}\right)^{\gamma-1}\cdot\frac{1}{\gamma}\frac{(V_3/V_2)^\gamma - 1}{(V_3/V_2) - 1}.$$

If we ignore the factor after the $\cdot$, this expression is the same as for the Otto cycle. The correction factor (after the $\cdot$) depends only on γ and the cutoff ratio V_3/V_2. To prove rigorously that it is always greater than 1 (given that $\gamma > 1$ and $V_3 > V_2$) is not easy, but this fact is clear from the plot at right, drawn for $\gamma = 7/5$. The efficiency of the Diesel cycle is therefore always less than that of the Otto cycle, for a given compression ratio. Note