

1. a. We just need to find the multiplicity  $g(E)$  and then calculate  $\sigma(E) = \ln g(E)$ . For a given  $E$ , we have  $n = E/\hbar\omega$  units of energy to distribute among  $N = 3$  oscillators. For low  $n$ , it is easy enough to just count the numbers of states.

We obtain:

- i.  $(n_x, n_y, n_z) = (0, 0, 0)$   
 $\sigma = \ln 1 = 0$
  - ii.  $(1, 0, 0)$  x 3 orders  
 $\sigma = \ln 3$
  - iii.  $(1, 1, 0)$  x 3 orders  
 $(2, 0, 0)$  x 3 orders  
 $\sigma = \ln 6$
  - iv.  $(1, 1, 1)$   
 $(2, 1, 0)$  x 6 orders  
 $(3, 0, 0)$  x 3 orders  
 $\sigma = \ln 10$
- b. The energy of the particle is most likely to change in a way that maximizes the total entropy of the particle and bath. The bath temperature  $\tau \equiv dE/d\sigma = \hbar\omega$  tells us that the entropy of the bath will increase by 1 if we transfer an energy  $\hbar\omega$  from the particle to the bath. The resulting decrease in entropy of the particle is  $\sigma(2\hbar\omega) - \sigma(\hbar\omega) = \ln(6/3) = \ln(2) < 1$ . (By contrast, if we transferred  $\hbar\omega$  of energy from the bath to the particle, then the entropy of the bath would decrease by 1, while the entropy of the particle would only increase by  $\sigma(3\hbar\omega) - \sigma(2\hbar\omega) = \ln(10/6) < 1$ .) Thus, the energy of the particle will tend to **decrease** by flowing to the bath to maximize the total entropy.
- c. The entropy of the particle will decrease, but the entropy of the bath will increase by more. Overall the entropy of the entire system will increase, consistent with the second law.
- d. The partition function for this 3D harmonic oscillator is  $Z = Z_1^3$ , where  $Z_1$  is the partition function for a single harmonic oscillator. Therefore,

$$\langle E \rangle = -\frac{\partial}{\partial \beta} \ln(Z_1^3) = -3 \frac{\partial}{\partial \beta} \ln(Z_1) = 3 \langle E_1 \rangle$$

The partition function of a single harmonic oscillator is given by

$$Z_1 = \sum_{n=0}^{\infty} e^{-n\hbar\omega\beta} = \frac{1}{1 - e^{-\hbar\omega\beta}}$$

So the average energy for a single harmonic oscillator is

$$\langle E_1 \rangle = -\frac{\partial}{\partial \beta} \ln Z_1 = \frac{\partial}{\partial \beta} \ln (1 - e^{-\hbar\omega\beta}) = \frac{-e^{-\hbar\omega\beta} \cdot -\hbar\omega}{1 - e^{-\hbar\omega\beta}} = \frac{\hbar\omega}{e^{\hbar\omega\beta} - 1}$$

Therefore the average energy for this 3D system is

$$\langle E \rangle = 3\langle E_1 \rangle = \frac{3\hbar\omega}{e^{\hbar\omega\beta} - 1} = \frac{3\hbar\omega}{e - 1} < 2\hbar\omega$$

Consistent with our prediction in part B, the energy decreased when the system was brought into thermal equilibrium.

2. a. We have  $N$  segments that can either point up or down, just like the  $N$  spins in a paramagnet. The total energy is  $E = -wL = -wl(n_\uparrow - n_\downarrow)$ , so the energy contribution of an individual link is  $\pm wl$ . Here, the total length  $L$  is analogous to the magnetization. They are both proportional to the spin excess  $n_\uparrow - n_\downarrow$ .

- b. The partition function is given by

$$Z = (e^{-wl/\tau} + e^{wl/\tau})^N$$

and the free energy is given by

$$F = -\tau \ln Z = -N\tau \ln (e^{-wl/\tau} + e^{wl/\tau})$$

- c. First, we can use the given fundamental thermodynamic relation for the energy to find the relation for the free energy,  $F = E - \tau\sigma$ .

$$\begin{aligned} dF &= dE - \tau d\sigma - \sigma d\tau \\ &= -Ldw - \sigma d\tau \end{aligned}$$

If  $\tau$  is constant, the last term is 0, and we can write

$$-\left(\frac{\partial F}{\partial w}\right)_\tau = L$$

- d. Combining our results from B and C,

$$\begin{aligned} L &= -\left(\frac{\partial F}{\partial w}\right)_\tau = -\frac{\partial}{\partial w}(-N\tau \ln (e^{-wl/\tau} + e^{wl/\tau})) \\ &= N\tau \cdot \frac{1}{e^{-wl/\tau} + e^{wl/\tau}} \cdot (-(l/\tau)e^{-wl/\tau} + (l/\tau)e^{wl/\tau}) \\ &= Nl \tanh \frac{wl}{\tau} \end{aligned}$$

e. Following the hint, we can write  $\mu$  as

$$\mu = L \left( \frac{\partial w}{\partial L} \right)_{\tau} = L \left( \frac{\partial L}{\partial w} \right)_{\tau}^{-1}$$

We can use our result from C to find  $(\partial L / \partial w)_{\tau}$ .

$$\left( \frac{\partial L}{\partial w} \right)_{\tau} = Nl \cdot \operatorname{sech}^2(wl/\tau) \cdot l/\tau$$

Plugging this and our result from C in, we get

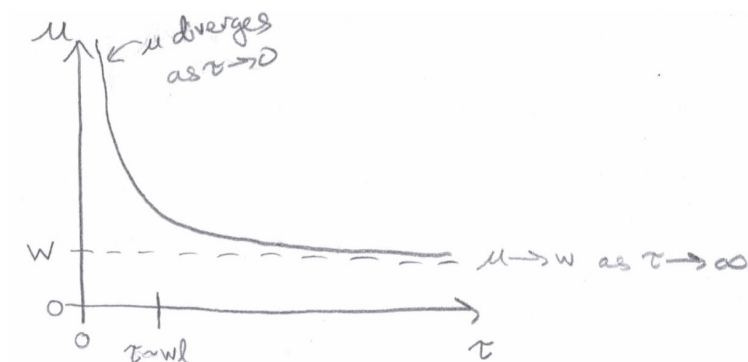
$$\begin{aligned} \mu &= Nl \tanh(wl/\tau) \cdot \frac{\tau}{Nl^2 \cdot \operatorname{sech}^2(wl/\tau)} \\ &= \frac{\tau}{l} \cdot \frac{\sinh(wl/\tau)}{\cosh(wl/\tau)} \cdot \cosh^2(wl/\tau) \\ &= \frac{\tau}{l} \sinh \frac{wl}{\tau} \cosh \frac{wl}{\tau} \\ &= \frac{\tau}{2l} \sinh \frac{2wl}{\tau} \end{aligned}$$

f. It is easier to find the limits by going back to exponentials.

$$\mu = \frac{\tau}{4l} (e^{2wl/\tau} - e^{-2wl/\tau})$$

As  $\tau \rightarrow 0$ , the second exponential term goes to 0, and the first exponential term goes to infinity. This dominates over the linear term that goes to 0, so overall  $\mu$  goes to infinity at low  $\tau$ . As  $\tau \rightarrow \infty$ ,  $2wl/\tau \rightarrow 0$ , so we can Taylor expand the exponentials to get

$$\mu \approx \frac{\tau}{4l} \left( 1 + \frac{2wl}{\tau} - \left( 1 - \frac{2wl}{\tau} \right) \right) = \frac{\tau}{4l} \cdot \frac{4wl}{\tau} = w$$



- g. At low  $\tau$ , the system will be very close to its lowest energy state, i.e., almost completely extended to the full length  $L = Nl$ . Thus, as  $\tau \rightarrow 0$ , it becomes increasingly difficult to stretch the rubber band any further. Correspondingly, the elastic modulus  $L(\partial w/\partial L)_\tau$ —quantifying the amount of additional force required to increase the length by a fixed fraction—diverges.
3. a. Since there is no potential energy in this system, we can just set  $\varepsilon$  equal to the kinetic energy to find  $v_n$ .

$$\varepsilon_n = \frac{n^2 \pi^2 \hbar^2}{2mL^2} = \frac{1}{2}mv_n^2, \text{ so } |v|_n = \frac{n\pi\hbar}{mL}$$

b.

$$\langle |v| \rangle = \sum_n v_n P_n = \sum_{n=1}^{\infty} \frac{n\pi\hbar}{mL} \cdot \frac{e^{-\varepsilon_n/\tau}}{Z} = \frac{\sum_n \frac{n\pi\hbar}{mL} e^{-\varepsilon_n/\tau}}{\sum_n e^{-\varepsilon_n/\tau}}$$

- c. The particle is in the classical regime if the temperature is much larger than the spacing between the energy levels, so  $\tau \gg (\pi^2 \hbar^2)/(2mL^2)$ . In this limit, the sums can be approximated as integrals. For the rest of this part, let's define this energy spacing to be  $\alpha \equiv \frac{\pi^2 \hbar^2}{2mL^2}$ , so  $E = \alpha n^2$ .

The partition function is given by

$$Z = \sum_{n=1}^{\infty} e^{-\varepsilon_n/\tau} \approx \frac{1}{2} \int_{-\infty}^{\infty} e^{-n^2 \alpha/\tau} dn = \frac{1}{2} \sqrt{\pi \cdot \frac{\tau}{\alpha}} = \frac{L}{h} \sqrt{2m\tau\pi}$$

The sum in the numerator is

$$\sum_{n=1}^{\infty} \frac{n\pi\hbar}{mL} e^{-\varepsilon_n/\tau} \approx \frac{\pi\hbar}{mL} \int_0^{\infty} n e^{-n^2 \alpha/\tau} dn = \frac{\pi\hbar}{mL} \cdot \frac{\tau}{2\alpha} \cdot -e^{-n^2 \alpha/\tau} \Big|_0^{\infty} = \frac{L\tau}{\pi\hbar}$$

Putting it all together, we find

$$\langle |v| \rangle = \frac{L\tau}{\pi\hbar} \cdot \frac{h}{L} \frac{1}{\sqrt{2m\tau\pi}} = \sqrt{\frac{2\tau}{m\pi}}$$

- d. We can find  $\langle v^2 \rangle$  from  $\langle E \rangle = m\langle v^2 \rangle/2$ , and we can find  $\langle E \rangle$  from the equipartition theorem. Since there is one degree of freedom,  $\langle E \rangle = \tau/2$ .

$$\begin{aligned} \langle v^2 \rangle &= \frac{2\langle E \rangle}{m} = \frac{\tau}{m} \\ \Delta v^2 &= \langle v^2 \rangle - \langle v \rangle^2 = \frac{\tau}{m} - \frac{2\tau}{m\pi} \\ \Delta v &= \sqrt{\frac{\tau}{m} \left(1 - \frac{2}{\pi}\right)} \end{aligned}$$

- e. i. In terms of the de Broglie wavelength, the partition function can be written as  $Z_L = L/\lambda_\tau$ , where  $\lambda_\tau = \frac{h}{\sqrt{2m\tau\pi}}$ . Then we can find the free energy

$$F_L = -\tau \ln Z_L = \tau(\ln \lambda_\tau - \ln L)$$
$$F_{2L} = -\tau \ln Z_{2L} = \tau(\ln \lambda_\tau - \ln L - \ln 2)$$

- ii. The work done on the system at constant temperature is the same as the change in the free energy, so the work done by the system is  $W = -\Delta F = \tau \ln 2$ . You can also find this by writing  $W = \int p dV$  and using  $pV = N\tau$ , with  $N = 1$ .
- iii. The energy of the ideal gas depends only on the temperature, so it doesn't change. Therefore the heat must be equal to the negative work on the system,  $\tau \ln 2$ . This also makes sense if you think about it in terms of phase space, because if the size of the system increases by 2, the multiplicity also then increases by 2. The entropy then increases by  $\ln 2$ , and the heat term is  $\tau \Delta \sigma = \tau \ln 2$ .