

Problem Set 7: SOLUTIONS

(1) An electrostatic potential.

$$P_{in} = \frac{1}{Z} e^{-E_{in}/\tau} \quad (\text{Boltzmann}).$$

$$Z = \sum_i e^{-E_i/\tau} = e^{-E_{in}/\tau} + e^{-E_{out}/\tau} \quad (\text{partition function}).$$

$$\text{Therefore } P_{in} = \frac{e^{-E_{in}/\tau}}{e^{-E_{in}/\tau} + e^{-E_{out}/\tau}} = \frac{1}{1 + e^{(E_{in} - E_{out})/\tau}}.$$

The difference in energy $E_{in} - E_{out} = qV$, where $V = 0.1$ Volts is the voltage, from elementary electrostatics. $\tau = k_B T$, where $k_B = 1.38 \times 10^{-23}$ J/K and $T = 310$ K = body

temperature. Therefore: $P_{in} = \frac{1}{1 + e^{qV/k_B T}}$. Note that if $V = 0$, $P_{in} = 1/2$, as we'd expect.

Plugging in numbers:
$$P_{in} = \frac{1}{1 + e^{1.6 \times 10^3 / 1.38 \times 310}} = 0.023.$$

Note that it's not correct to simply say $P_{in} = e^{-qV/k_B T}$ [*wrong*], though numerically this is almost correct. Why?

(2) The CO₂ molecule, revisited.

For a particular mode "m",
$$r_m = \frac{P_{n=2}}{P_{n=1}} = \frac{e^{-E_2/\tau}}{e^{-E_1/\tau}} = \frac{e^{-(3/2)hf_m/\tau}}{e^{-(1/2)hf_m/\tau}} = e^{-hf_m/\tau},$$
 where f_m

is the normal mode frequency. From this, $-\ln(r_m) = \frac{hf_m}{\tau}$, and $\tau = -\frac{hf_m}{\ln(r_m)}$.

[INITIAL VERSION OF THE PROBLEM] Unfortunately, as written, this expression can be evaluated for each of the normal modes separately, giving two **different** temperatures. This isn't

physically realistic, and it's my fault for mis-writing the problem. If you solved the problem this way, you won't be penalized for it. You would have found: $\tau_1 = 834$ K and $\tau_2 = 367$ K.

[REVISED VERSION OF THE PROBLEM] The **ratio** of the r values of the two modes is

$$\frac{r_2}{r_1} = \frac{\exp\left(-hf_2/\tau\right)}{\exp\left(-hf_1/\tau\right)} = \exp\left(-h(f_2 - f_1)/\tau\right). \quad \text{We are told that the ratio is } r_{mode1}/r_{mode2} = 5.8, \text{ so:}$$

$$\tau = \frac{h(f_2 - f_1)}{\ln\left(r_1/r_2\right)} = \frac{6.63 \times 30.5 \times 10^{-22} [\text{Joules}]}{\ln(5.8)} = k_B T, \text{ from which } T = 832 \text{ K.}$$

(3, 4 pts.) The Partition Function.

The partition function $Z = \sum_i \exp\left(-\frac{E_i}{\tau}\right)$, where the sum is over states. The probability of state i is

$$p_i = \frac{1}{Z} \exp\left(-\frac{E_i}{\tau}\right) = \frac{\exp\left(-\frac{E_i}{\tau}\right)}{\sum_i \exp\left(-\frac{E_i}{\tau}\right)}.$$

Let's call the ground state energy E_0 ; we can factor this out, if we want:

$$Z = \sum_i \exp\left(-\frac{E_i}{\tau}\right) = \exp\left(-\frac{E_0}{\tau}\right) \sum_i \exp\left(-\frac{E_i - E_0}{\tau}\right)$$

$$p_i = \frac{1}{Z} \exp\left(-\frac{E_i}{\tau}\right) = \frac{\exp\left(-\frac{E_0}{\tau}\right) \exp\left(-\frac{E_i - E_0}{\tau}\right)}{\exp\left(-\frac{E_0}{\tau}\right) \sum_i \exp\left(-\frac{E_i - E_0}{\tau}\right)} = \frac{\exp\left(-\frac{E_i - E_0}{\tau}\right)}{\sum_i \exp\left(-\frac{E_i - E_0}{\tau}\right)}.$$

(a) In the high temperature limit ($\tau \rightarrow \infty$), the probability of any state i is

$$p_i = \frac{\exp\left(-\frac{E_i - E_0}{\tau}\right)}{\sum_i \exp\left(-\frac{E_i - E_0}{\tau}\right)} \rightarrow \frac{1}{\sum_i 1} = \frac{1}{Q}, \text{ i.e. each state is equally likely, with probability } \frac{1}{Q}.$$

partition function $Z = \sum_i \exp\left(-\frac{E_i}{\tau}\right) \rightarrow \sum_i 1 = Q$. There's a subtlety here: Strictly, I can only

say that $\frac{\tau}{E_i - E_0} \rightarrow \infty$, since I could always add an arbitrary constant to all the energies. So

really, all I can show is that

$Z = \exp\left(\frac{-E_0}{\tau}\right) \sum_i \exp\left(-\frac{E_i - E_0}{\tau}\right) \rightarrow \exp\left(\frac{-E_0}{\tau}\right) \sum_i 1 = \exp\left(\frac{-E_0}{\tau}\right) Q$. If we define $E_0 \equiv 0$, we can state $Z \rightarrow Q$. Either answer is fine.

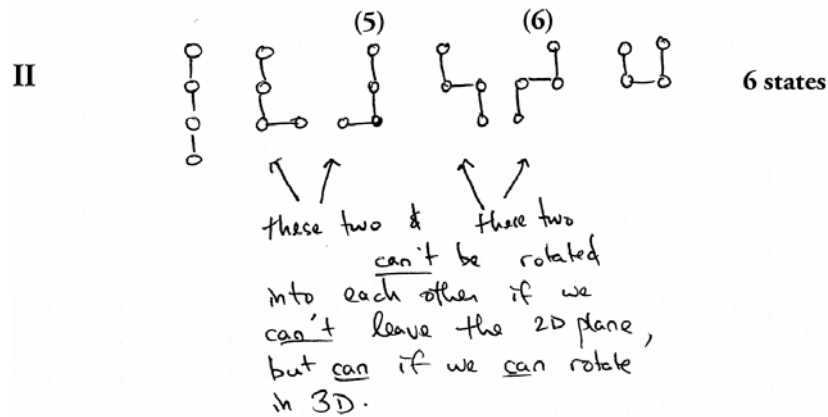
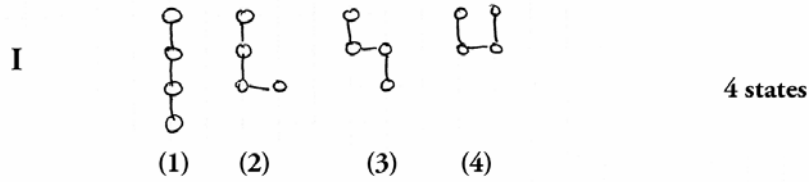
(b) In the zero temperature limit, let's think about $p_i = \frac{\exp\left(-\frac{E_i - E_0}{\tau}\right)}{\sum_i \exp\left(-\frac{E_i - E_0}{\tau}\right)}$. All the $E_i - E_0$ are >0

except for the ground state; for all these, $\exp\left(-\frac{E_i - E_0}{\tau}\right) \rightarrow 0$. For the ground state,

$E_i - E_0 = 0$, so $\exp\left(-\frac{E_i - E_0}{\tau}\right) \rightarrow 1$. Therefore, the probability of being in the ground state $\rightarrow 1$, and all others go to zero. Similarly, only the ground state term in Z is nonzero, and this is $Z \rightarrow \exp\left(\frac{-E_0}{\tau}\right)$. If we define $E_0 \equiv 0$, we can state $Z \rightarrow 1$. Either answer is fine.

(4) A four-bead polymer chain.

(a) Unintentionally, there are two valid interpretations of this problem. We can say that there are **four** distinct states – (1) through (4) below. Or we can say that there are **six** distinct states (1) through (6) below. States (2) and (5) are **equivalent** under a rotation into the third dimension, and so I had intended that they not be considered as distinct. However, as written the problem implies that our 2D polymer should really stay in two dimensions, and so we can't rotate from (2) to (5). (The same logic holds for (3) and (6). But note that no “mirror image” of (4) is different from (4), in any interpretation.) These two interpretations will lead to **different** answers – which highlights the importance in real life of knowing what symmetries apply to systems of interest. Due to the ambiguity of the problem, **either interpretation will be considered correct**. Congratulations to those of you who noticed this!



The energies $E = \varepsilon/d^2$.

state	d	E
1	3	$\varepsilon/9$
2	$\sqrt{5}$	$\varepsilon/5$
3	$\sqrt{5}$	$\varepsilon/5$
4	1	ε
5	$\sqrt{5}$	$\varepsilon/5$
6	$\sqrt{5}$	$\varepsilon/5$

(b) If we don't consider (5) and (6)

d	degeneracy
1	1
$\sqrt{5}$	2
3	1

If we do consider (5) and (6)

d	degeneracy
1	1
$\sqrt{5}$	4
3	1

(c)

(c) no considering (5) & (6) $p_i = \frac{1}{Z} e^{-\beta E_i}$

$$\langle d \rangle = (1 \times e^{-\frac{\epsilon}{kT}} + 2 \times \sqrt{5} \times e^{-\frac{\epsilon}{5kT}} + 3 \times e^{-\frac{\epsilon}{9kT}}) / (e^{-\frac{\epsilon}{kT}} + 2e^{-\frac{\epsilon}{5kT}} + e^{-\frac{\epsilon}{9kT}})$$

if consider (5) & (6)

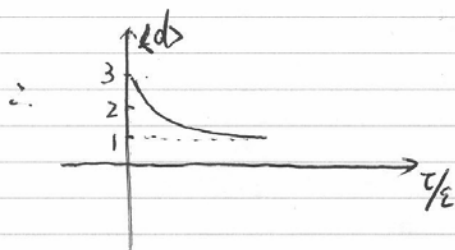
$$\langle d \rangle = (1 \times e^{-\frac{\epsilon}{kT}} + 4 \times \sqrt{5} \times e^{-\frac{\epsilon}{5kT}} + 3 \times e^{-\frac{\epsilon}{9kT}}) / (e^{-\frac{\epsilon}{kT}} + 4e^{-\frac{\epsilon}{5kT}} + e^{-\frac{\epsilon}{9kT}})$$

set $u = \frac{\epsilon}{kT}$

$$\text{then } \langle d \rangle = \frac{e^{-\frac{1}{ku}} + 2\sqrt{5}e^{-\frac{1}{5ku}} + 3e^{-\frac{1}{9ku}}}{e^{-\frac{1}{ku}} + 2e^{-\frac{1}{5ku}} + e^{-\frac{1}{9ku}}}$$

as $u \rightarrow 0$ $\langle d \rangle \rightarrow 3$

as $u \rightarrow \infty$ $\langle d \rangle \rightarrow 1$



(5) Paramagnetism and the Curie Law.

We have showed that for non-interacting binary spins, with $|s| \ll N$, the entropy

$\sigma = N \ln 2 - \frac{s^2}{2N} = N \ln 2 - \frac{E^2}{2\epsilon^2 N}$. We have shown that in general, temperature, energy, and

entropy are related by $\tau^{-1} = \left. \frac{\partial \sigma}{\partial E} \right|_{N,V}$. Therefore, $\tau^{-1} = \frac{E}{\epsilon^2 N} = \frac{s}{\epsilon N}$. (We've used $E = s\epsilon$ several

times.) The s given by the preceding relation is the equilibrium expectation value of the spin excess

– it's the most likely configuration of the spin system! $M = \frac{\langle s \rangle}{N}$, and $\epsilon = mB$ (as given in the

problem) so we can write the last relation as $\tau^{-1} = \frac{E}{\epsilon^2 N} = \frac{M}{mB}$, i.e. $M = \frac{mB}{\tau}$.

(6) Calibrating an optical trap.

(a) $\langle x \rangle = \sum_i x_i p_i$, where our p_i satisfy (as you can check) $\sum_i p_i = 1$. Plugging in numbers, $\langle x \rangle = 0.0212 \mu\text{m}$. This is the location of the trap center.

(b)

It might first occur to us to plot $p(x)$ vs x :

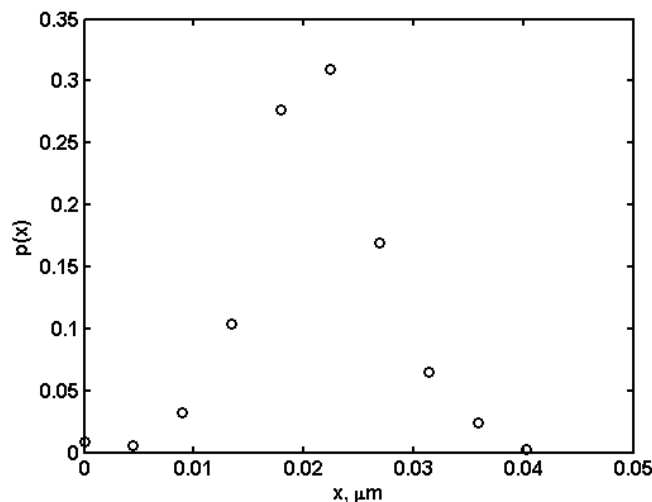


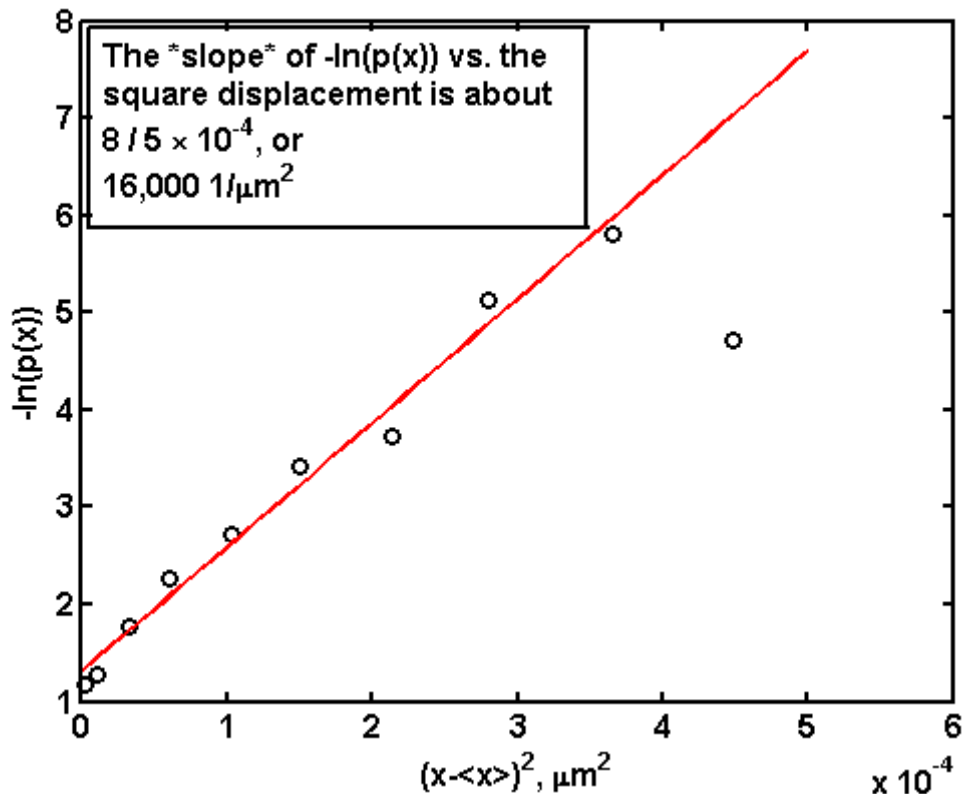
Figure 6.1. $p(x)$ vs. x

It's not immediately obvious where this gets us! So let's think: What do we expect $p(x)$ for a spring-like energy function to look like? DON'T FORGET THAT "X" IN HOOKE'S LAW REFERS TO DISPLACEMENT FROM THE EQUILIBRIUM POSITIONS! From the

Boltzmann relation, we expect $p(x) \propto \exp[-U(x)/\tau] = \exp\left[-\frac{k(x-\langle x \rangle)^2}{2\tau}\right]$, i.e. a Gaussian

function centered at the equilibrium position. We could try fitting the above plot to a Gaussian, but let's try to think more:

Taking the log of both sides, we get $\ln(p(x)) = \ln(const) - \frac{k(x-\langle x \rangle)^2}{2\tau}$, i.e. a parabola. (The constant comes from the constant of proportionality above.) This sounds more tractable. Can we find a linear relation? If we plot $-\ln(p(x))$ versus $(x-\langle x \rangle)^2$, we should get a **straight line** whose slope is $\frac{k}{2\tau}$. This sounds great, since it's easy to "read off" the slope from a line. Let's try:



The data points fit the expected linear relation very well. (One point doesn't fit, but no one ever said real life was pretty. Incidentally, which data points would you 'expect' based on Figure 6.1 and the graph in the assignment to be the least reliable?) In the "plotted" units, we can read the slope

"by eye" as about 16,000 $1/\mu\text{m}^2$. Therefore $\frac{k}{2\tau} = 16000 \frac{1}{\mu\text{m}^2}$, and

$k = 32000 \frac{1}{(\mu\text{m})^2} \times 296\text{K} \times 1.38 \times 10^{-23} \text{J/K}$, i.e. $k = 1.3 \times 10^{-4} \text{N/m}$. This is the stiffness of our optical "spring."

This is how we, and others, determine the stiffness of optical traps. Note that we don't have to know anything about optics or the mechanism by which light and matter interact – the Boltzmann relation spares us all this. The **only** thing that we need to know to determine probabilities is the energy!