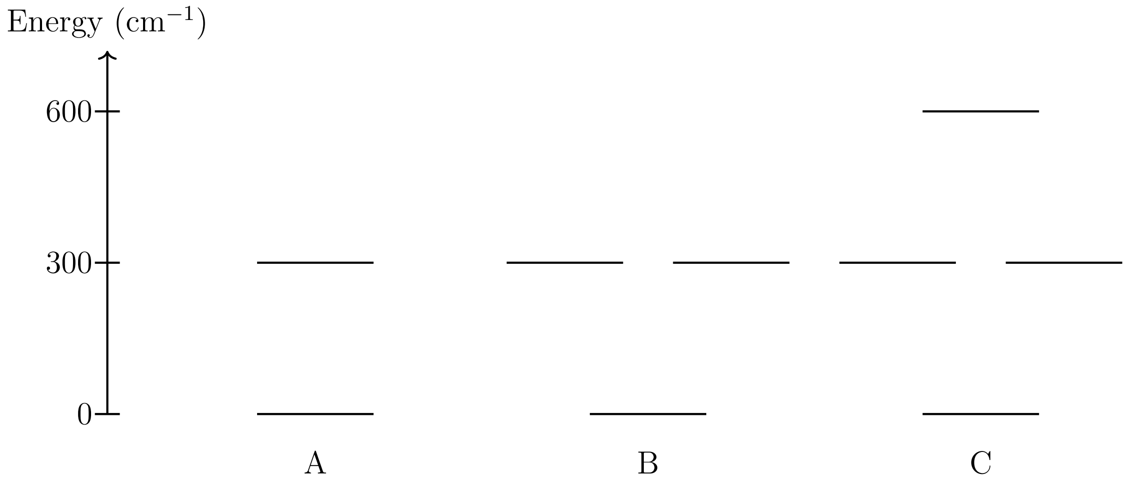
1. Consider the following three systems



(a) For energy level diagram A, if the probability of being in the 300 cm^{-1} level is 0.15, what is the temperature of the system?

$$Q = \sum_i e^{-\beta E_i} = 1 + e^{-300/(0.695T)}$$
$$0.15 = \frac{e^{-300/(0.695T)}}{1 + e^{-300/(0.695T)}}$$
$$0.15 = 0.85\, e^{-300/(0.695T)}$$
$$\ln\left(\frac{0.15}{0.85}\right) = \frac{-300}{0.695T}$$
$$T = 249 \text{ K}$$

(b) For energy level diagram B, if the probability of being in the 300 cm^{-1} level is 0.15, what is the temperature of the system? Explain in at most two sentences why this is the same, higher, or lower temperature as you found in part a.

$$Q = \sum_i e^{-\beta E_i} = 1 + 2e^{-300/(0.695T)}$$
$$0.15 = \frac{2e^{-300/(0.695T)}}{1 + 2e^{-300/(0.695T)}}$$
$$0.15 + 0.3\, e^{-300/(0.695T)} = 2\, e^{-300/(0.695T)}$$
$$0.15 = 1.7\, e^{-300/(0.695T)}$$
$$e^{-300/(0.695T)} = \frac{0.15}{1.7}$$
$$-\frac{300}{0.695T} = \ln\left(\frac{0.15}{1.7}\right) \implies T = 178 \text{ K}$$

Degeneracy makes the state more likely, so lower temperature is needed

(c) For energy level diagram C, if the probability of being in the 300 cm^{-1} is 0.15, how does its temperature compare (higher, lower, the same) to what you found in part b? You can approach this mathematically or conceptually.

At the same temp, the population is lower since the higher state draws probability away from the 300 cm^{-1} state. This means to maintain 0.15, the temperature must increase.

$$0.15 = \frac{2e^{-300/(0.695T)}}{1 + 2e^{-300/(0.695T)} + e^{-600/(0.695T)}} \implies 0.15 = \frac{2x}{1+2x+x^2} \qquad x = e^{-300/(0.695T)}$$

$$0.15 = \frac{2x}{1+2x+x^2}$$

$$0.15x^2 - 1.7x + 0.15 = 0$$

$$x = \frac{-(-1.7) \pm \sqrt{(-1.7)^2 - 4(0.15)(0.15)}}{2(0.15)} \approx \cancel{11.23} \quad \text{or} \quad 0.1$$

$$T = -\frac{300}{0.695\ln(0.1)} \approx 187\text{ K}$$

(d) For diagram C, what temperature is required for the probability of being in the 300 cm^{-1} level to be 0.5?

This means $P_{\text{not }300} = 0.5$, all states are equally likely, which occurs at $T \to \infty$.

$$0.50 = \frac{2x}{1+2x+x^2} \qquad x = e^{-300/(0.695T)}$$

$$0.50(1+2x+x^2) = 2x \implies 0.50x^2 - 1.0x + 0.50 = 0$$

$$x^2 - 2x + 1 = 0 \implies (x-1)^2 = 0 \implies x = 1$$

$$e^{-300/(0.695T)} = 1 \implies -\frac{300}{0.695T} = 0 \implies T \to \infty$$

2. Calculate the fraction of lithium atoms in the first excited state at 300 K, 1000 K, 2000 K. Does your answer match the trend you'd expect with increasing temperature?

Atom	Config	Term	$g = 2J+1$	E / cm^{-1}
Li	$1s^22s$	$^2S_{1/2}$	2	0
	$1s^22p$	$^2P_{1/2}$	2	14 903.66
		$^2P_{3/2}$	4	14 904.00
	$1s^23s$	$^2S_{1/2}$	2	27 206.12

The first excited state is $^2P_{1/2}$ with $g_1 = 2$. We use $k_B = 0.695\ \text{cm}^{-1}/\text{K}$:

$$q = 2 + 2e^{-\beta E_1} + 4e^{-\beta E_2} + 2e^{-\beta E_3}$$

$$P_1 = \frac{2e^{-\beta E_1}}{q} = \frac{e^{-E_1/k_BT}}{1 + e^{-E_1/k_BT} + 2e^{-E_2/k_BT} + e^{-E_3/k_BT}}$$

At 300 K: $q \approx 2.000 \implies P_1 = \boxed{1.5 \times 10^{-31}}$

At 1000 K: $q \approx 2.000 \implies P_1 = \boxed{4.9 \times 10^{-10}}$

At 2000 K: $q \approx 2.000 \implies P_1 = \boxed{2.2 \times 10^{-5}}$

The fraction increases with temperature as expected, since more thermal energy means more excitations

Homework Problem 7

1. In statistical mechanics, the exact value of energy E is not physically meaningful, only relative energy differences matter. This allows us to set the ground state energy at $\varepsilon_0 = 0$ for convenience. Show that pressure is independent of the choice of zero energy.
   Hint: Consider shifting all energy levels by a constant E_0, i.e., $E_i' = E_i + E_0$. How would this affect the expression for pressure?