

# E<sup>3</sup>E Homework #8

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## ① Boltzmann Probabilities

a) If we have infinite temperature, we know that we will also have an infinitely large entropy as well. Infinite entropy means that all states are equally probable. We have 3 states; each state has a 33% probability (1/3 chance).

$$P_i = \frac{e^{-\beta \varepsilon_i}}{e^{-\beta \varepsilon_1} + e^{-\beta \varepsilon_2} + e^{-\beta \varepsilon_3}} \rightarrow \text{As } T \rightarrow \infty \rightarrow \beta = \frac{1}{kT} \rightarrow 0 \rightarrow P_i = \frac{e^{0}}{e^{0} + 1 + e^{0}} \rightarrow P_i = \frac{1}{1+1+1} = \frac{1}{3}$$

$z = \sum e^{\beta E_i}$   $\uparrow$

With this, we can find internal energy (U).

$$U = \sum P E_i \rightarrow U = \frac{1}{3}(-\varepsilon_1) + 0 + \frac{1}{3}(\varepsilon_2) + 0 \rightarrow U = 0$$

And last, we can solve for entropy (S).

$$S = -k_B \sum P \ln(P) \rightarrow S = -k_B \left( \frac{1}{3} \ln\left(\frac{1}{3}\right) + \frac{1}{3} \ln\left(\frac{1}{3}\right) + \frac{1}{3} \ln\left(\frac{1}{3}\right) \right)$$

$$S = -k_B (1) \ln\left(\frac{1}{3}\right) \rightarrow S = 1.52 \times 10^{-23} \text{ J/K}$$

## ① Boltzmann Probability

b) Opposite to high temp, when we have low temperature the probability of being in a lower state is much higher because the entropy is proportionally low. Thus we are most likely to find a particle in the lowest state ( $-\varepsilon$ ), a bit less likely to find it in the second lowest (0), and not likely to find it in the third state ( $+\varepsilon$ ).

$$P_{-\varepsilon} = \frac{e^{-\beta\varepsilon}}{e^{-\beta\varepsilon} + 1 + e^{\beta\varepsilon}} \rightarrow P_{-\varepsilon} = \frac{e^{-\beta\varepsilon}}{e^{\beta\varepsilon} + 1 + e^{-\beta\varepsilon}} \left( \frac{e^{-\beta\varepsilon}}{e^{-\beta\varepsilon}} \right) \rightarrow P_{-\varepsilon} = \frac{e^{-\beta\varepsilon}}{e^{-2\beta\varepsilon} + e^{-\beta\varepsilon} + 1}$$

$z = \sum e^{\beta E_i}$   $\uparrow$  real small  $\uparrow$  small  $\uparrow$

Since  $T \rightarrow \sim 0$  and  $\beta = \frac{1}{k_B T} \rightarrow P_{-\varepsilon} = \frac{e^{-\beta\varepsilon}}{(\sim 1)} \rightarrow$  very small number

$$P_0 = \frac{e^{-\beta(0)}}{e^{-\beta\varepsilon} + 1 + e^{\beta\varepsilon}} \rightarrow P_0 = \frac{e^{(0)}}{e^{\beta\varepsilon} + 1 + e^{-\beta\varepsilon}} \left( \frac{e^{-\beta\varepsilon}}{e^{-\beta\varepsilon}} \right) \rightarrow P_0 = \frac{(1)(e^{-\beta\varepsilon})}{e^{-2\beta\varepsilon} + e^{-\beta\varepsilon} + 1}$$

$z = \sum e^{\beta E_i}$   $\uparrow$  real small  $\uparrow$  small  $\uparrow$

Since  $T \ll 1$  and  $\beta = \frac{1}{k_B T} \rightarrow P_0 = \frac{e^{-\beta\varepsilon}}{(\sim 1)} \rightarrow$  small number

# ① Boltzmann Probabilities Cont.

$$P_{\varepsilon} = \frac{e^{-\beta(\varepsilon)}}{e^{-\beta(\varepsilon)} + 1 + e^{\beta(\varepsilon)}} \rightarrow P_{\varepsilon} = \frac{e^{\beta\varepsilon}}{e^{-\beta\varepsilon} + 1 + e^{\beta\varepsilon}} \left( \frac{e^{-\beta\varepsilon}}{e^{-\beta\varepsilon}} \right) \rightarrow P_{\varepsilon} = \frac{e^{(\alpha)}}{e^{-2\beta\varepsilon} + e^{-\beta\varepsilon} + 1}$$

$z = \sum e^{\beta E_i}$   $\uparrow$  real small  $\uparrow$   $\uparrow$  small

Since  $T \ll 1$  and  $\beta = \frac{1}{k_B T} \rightarrow P_{\varepsilon} = \frac{(1)}{(\sim 1)} \rightarrow$  Almost 1  
(slightly more)

Thus, we can see  $0 < P_{\varepsilon} < P_0 < P_{-\varepsilon}$

c) Now, if  $T$  is exactly 0, then we should only see particles in the lowest state since entropy is so low. Thus, we should have 100% probability to find one in state  $-\varepsilon$  and 0% everywhere else.

Since  $T=0$  the  $\lim_{T \rightarrow 0}(\beta) = \frac{1}{k_B(0)} = \infty$ . So,

$$P_{\varepsilon} = \frac{e^{-(\infty)\varepsilon}}{e^{-(\infty)\varepsilon} + 1 + e^{(\infty)\varepsilon}} \rightarrow P_{\varepsilon} = \frac{e^{-\infty}}{e^{-\infty} + 1 + e^{\infty}} \left( \frac{e^{-\beta\varepsilon}}{e^{-\beta\varepsilon}} \right) \rightarrow P_{\varepsilon} = \frac{e^{-\infty}}{e^{-\infty} + e^{-\infty} + 1}$$

$z = \sum e^{\beta E_i}$   $\uparrow$  zero  $\uparrow$  zero  $\uparrow$

$$P_{\varepsilon} = \frac{(0)}{(1)} \rightarrow P_{\varepsilon} = 0$$

# ① Boltzmann Probabilities

$$P_0 = \frac{e^{-(\infty)\varepsilon}}{e^{-(\infty)\varepsilon} + 1 + e^{(\infty)\varepsilon}} \rightarrow P_0 = \frac{e^0}{e^{-\infty} + 1 + e^{\infty}} \left( \frac{e^{-\infty}}{e^{-\infty}} \right) \rightarrow P_0 = \frac{e^{-\infty}}{e^{-2\infty} + e^{-\infty} + 1}$$

*zero* *zero* *zero*

$z = \sum e^{\beta E_i}$

$$P_0 = \frac{(0)}{(0) + (0) + 1} \rightarrow P_0 = \frac{0}{1} \rightarrow \boxed{P_0 = 0}$$

$$P_{\varepsilon} = \frac{e^{-(\infty)(-\varepsilon)}}{e^{-(\infty)(-\varepsilon)} + 1 + e^{(\infty)(-\varepsilon)}} \rightarrow P_{\varepsilon} = \frac{e^{\infty}}{e^{-\infty} + 1 + e^{\infty}} \left( \frac{e^{-\beta\varepsilon}}{e^{-\beta\varepsilon}} \right) \rightarrow P_{\varepsilon} = \frac{(1)}{e^{-2\infty} + e^{-\infty} + 1}$$

*zero* *zero* *zero*

$z = \sum e^{\beta E_i}$

$$P_{\varepsilon} = \frac{(1)}{(1)} \rightarrow \boxed{P_{\varepsilon} = 1}$$

With this, we can calculate internal energy ( $U$ )

$$U = 1(-\varepsilon) + 0(0) + 0(\varepsilon) \rightarrow \boxed{U = -\varepsilon}$$

Now, we can solve for entropy ( $S$ )

$$S = -k_B \sum P \ln(P) \rightarrow S = k_B ((1) \ln(1) + (0) \ln(0) + (0) \ln(0))$$

$$S = k_B(0) \rightarrow \boxed{S = 0}$$

## ① Boltzmann Probabilities

d) Let's just plug and chugg a situation where  $T$  is negative.

Let  $T = -C$  where  $C$  is const.  $\rightarrow \beta = \frac{1}{k(-C)} \rightarrow \beta = -\frac{1}{C}$

$$P_{\epsilon} = \frac{e^{-(\beta)\epsilon}}{e^{-(\beta)\epsilon} + 1 + e^{(\beta)\epsilon}} \rightarrow P_{\epsilon} = \frac{e^{\beta\epsilon}}{e^{\beta\epsilon} + 1 + e^{-\beta\epsilon}} = \frac{e^{\beta\epsilon}}{e^{-\beta\epsilon} + 1 + e^{\beta\epsilon}} = P_{-\epsilon}$$

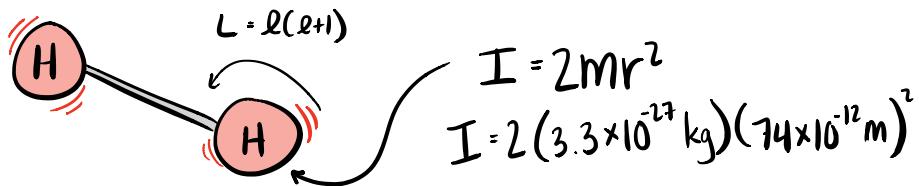
$z = \sum e^{\beta E_i}$   $\uparrow$

So, I guess making  $T$  negative gives us an expression equal to the probability of  $-\epsilon$  when we plug it into our  $P_{\epsilon}$  equation. Further we get the reverse when plugging it into our  $P_{-\epsilon}$  equation. So, changing the sign of  $T$  must give us the probability of the opposite state.

## ② Diatomic Hydrogen

$$H = \frac{1}{2I} L^2 \text{ with eigenvalues } E_{\text{em}} = \hbar^2 \frac{\ell(\ell+1)}{2I}$$

a) Find Ground, first, and second State energies.



For  $\ell, m = 0$  (Ground State)  $\rightarrow E_{(0)(0)} = \frac{\hbar^2}{2I}(0)(0+1) = \boxed{0}$

For  $\ell = 1, m = -1, 0, 1$ :

$$E_{(1)(1)} = E_{(1)(0)} = E_{(1)(-1)} = \frac{\hbar^2}{2I}(1)(1+1) = \frac{\hbar^2}{2I}(2) = \frac{\hbar^2}{I} = \frac{\hbar^2}{(2mr^2)} = \boxed{\frac{\hbar^2}{4.61 \times 10^{-47}}}$$

For  $\ell = 2, m = -2, -1, 0, 1, 2$ :

$$E_{(2)(2)} = E_{(2)(1)} = E_{(2)(0)} = E_{(2)(-1)} = E_{(2)(-2)} = \frac{\hbar^2}{2I}(2)(2+1) = \frac{\hbar^2}{2I}(6) = \frac{\hbar^2 3}{I}$$

$$E_{\ell=2} = \frac{\hbar^2 3}{I} \rightarrow \frac{\hbar^2 3}{2(2mr^2)} \rightarrow \boxed{\frac{\hbar^2}{7.23 \times 10^{-47}}}$$

## ② Diatomic Hydrogen cont.

b) Find relative probability of H-molecule in  $\ell=0$ .

At room Temperature  $T$ , probability of finding H in state with energy  $E$  is

$$P_i = \frac{P_{00}}{P_{11} + P_{10} + P_{01}} \rightarrow P_i = \frac{e^{-\beta E_i}}{Z} \rightarrow Z = \sum_i e^{-\beta E_i}$$

$$P_{00} = \frac{1}{3e^{\frac{-\beta k_B^2}{T}}}$$

OR

$$P(E_i) = \frac{e^{-\beta E_i}}{\sum_i g_i e^{-\beta E_i}} \rightarrow P(E_i) = \frac{e^{-\beta(0)}}{\left(e^{\frac{-\beta k_B^2}{T}} + e^{\frac{-\beta k_B^2}{T}} + e^{\frac{\beta k_B^2}{T}}\right)} \rightarrow P_{00} = 0.355$$

c) Find temperature at this ratio.

$$P_{00} = 1 \rightarrow 1 = \frac{e^{\frac{\beta k_B^2}{T}}}{3} \rightarrow 3 = e^{\frac{\beta k_B^2}{T}} \rightarrow \ln(3) = \frac{\beta k_B^2}{T}$$

we know that  $\beta = \frac{1}{k_B T}$ . So we can plug into our stuff

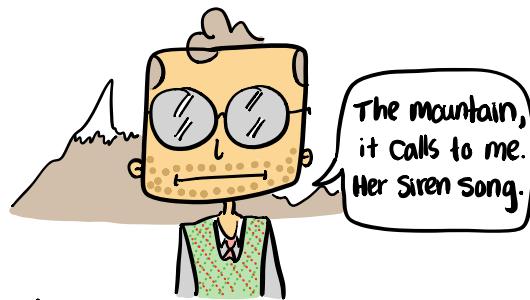
$$\ln(3) = \left(\frac{1}{k_B T}\right) \left(\frac{k_B^2}{T}\right) \rightarrow T = \frac{k_B^2}{k_B \ln(3)} \rightarrow T = \frac{k_B^2}{(4.61 \times 10^{-3})(k_B) \ln(3)} \frac{(J \cdot s)^2}{kg \cdot m^2 \left(\frac{1}{K}\right)}$$

$$T = 15.77 \quad \frac{J \cdot s^2}{kg \cdot m^2 \left(\frac{1}{K}\right)} \quad \frac{s^2}{kg \cdot m^2} = \frac{1}{J} \quad \frac{1}{\left(\frac{1}{K}\right)} = K$$

At this temp, the ratio will be 1.

## ② Diatomic Hydrogen Cont.

d) Find probability at  $l=2$ .



$$P_i = \frac{P_{00}}{P_{2-2} + P_{2-1} + P_{22}} \rightarrow \frac{(e^0)}{e^{-\frac{3\beta k^2}{I}} + e^{-\frac{3\beta k^2}{I}} + e^{-\frac{3\beta k^2}{I}} + e^{-\frac{3\beta k^2}{I}} + e^{-\frac{3\beta k^2}{I}}}$$

$$P_i = \frac{1}{5 e^{-\frac{3\beta k^2}{I}}} \leftarrow M = \{-2, -1, 0, 1, 2\} \rightarrow 5$$

$$P_i = \frac{e^{-\frac{3\beta k^2}{I}}}{5} \rightarrow P_i = \frac{e^{-\left(\frac{3}{(1.38 \times 10^{-23} \frac{J}{K})(293.15K)}\right) \frac{(1.055 \times 10^{-34} J \cdot s)^2}{(4.61 \times 10^{-47} \text{kg} \cdot m^2)}}}{5}$$

$$P_i = \frac{(1.7)}{5} \frac{\frac{J \cdot s^2}{\text{kg} \cdot \text{m}^2}}{\cancel{\frac{J \cdot s^2}{\text{kg} \cdot \text{m}^2}}} \rightarrow P_i = 0.34 \quad \text{Probability at } l=2$$

$\frac{s^2}{\text{kg} \cdot \text{m}^2} = \frac{1}{J}$

### ③ Gas in the Atmosphere

a) Since we are asked for the relative probability, we can set up an eigenstate probability ratio between  $P_{\text{space}}$  and  $P_{\text{curvo}}$ . We can do this because we know the eigenstates themselves are the same between these two places.

$$\frac{P_{\text{space}}}{P_{\text{curvo}}} = \frac{e^{-\beta(E - \frac{GMm}{r_{\text{space}}})}}{e^{-\beta(E - \frac{GMm}{r_{\text{curvo}}})}}$$

S
e<sup>-\beta E</sup>(e<sup>\frac{\beta GMm}{r\_{\text{space}}}</sup>)
e<sup>\beta \frac{GMm}{r\_{\text{space}}}</sup>

Now,  $r_{\text{space}} \gg r_{\text{curvo}}$ . It's so big let's approximate it to  $\infty$ . Then we can say,

$$e^{\frac{1}{r_{\text{space}}}} \rightarrow e^{\frac{1}{(\infty)}} \rightarrow e^{(0)} \rightarrow (1)$$

And, plugging this back in, we can say

$$P_N = \left( e^{\frac{\beta GMm}{r_{\text{space}}}} \right) e^{-\beta \frac{GMm}{r_{\text{curvo}}}} \rightarrow P_N = \frac{(1)}{e^{\beta \frac{GMm}{r_{\text{curvo}}}}} \rightarrow P_N = e^{-\frac{\beta GMm}{r_{\text{curvo}}}}$$

Where  $M$  is mass of the Earth =  $5.972 \times 10^{24}$  kg  
 Where  $m$  is mass of Nitrogen =  $4.65 \times 10^{-26}$  kg

### ③ Gas in the Atmosphere Cont.

where  $G$  is the Gravitational const =  $6.67 \times 10^{-11} \frac{\text{N} \cdot \text{m}^2}{\text{kg}^2}$   
 and where  $r_{\text{Corvo}}$  is the radius of the Earth center to Corvallis, OR =  $6.371 \times 10^6 \text{ m}$

We can plug in for numerical answer.  $T = 293.15 \text{ K}$

$$P_N = e^{-\left(\frac{1}{(1.38 \times 10^{-23} \frac{\text{J}}{\text{K}})(293.15 \text{ K})}\right) \left(\frac{(6.67 \times 10^{-11} \frac{\text{N} \cdot \text{m}^2}{\text{kg}^2})(5.97 \times 10^{24} \text{ kg})(4.65 \times 10^{26} \text{ kg})}{(6.371 \times 10^6 \text{ m})}\right)}$$

Wolfram Alpha  $\rightarrow$   $P_N = 9.89 \times 10^{-313}$

We can repeat the same process as before but plugging in values for Oxygen.

$$P_O = e^{-\frac{BGMm}{r_{\text{Corvo}}}}$$
 where  $m = 5.31 \times 10^{-26} \text{ kg}$  and all other variables are kept the same

$$P_O = e^{-\left(\frac{1}{(1.38 \times 10^{-23} \frac{\text{J}}{\text{K}})(293.15 \text{ K})}\right) \left(\frac{(6.67 \times 10^{-11} \frac{\text{N} \cdot \text{m}^2}{\text{kg}^2})(5.97 \times 10^{24} \text{ kg})(5.31 \times 10^{-26} \text{ kg})}{(6.371 \times 10^6 \text{ m})}\right)}$$

Wolfram Alpha  $\rightarrow$   $P_O = e^{-810.39}$  Larger than N

### ③ Gas in the atmosphere cont.

We can repeat the same process as before but plugging in values for He.

$P_{He} = e^{-\frac{GMm}{r_{\text{curvo}}}}$  where  $M = 6.64 \times 10^{-27} \text{ kg}$  and all other variables are kept the same.

$$P_{He} = e^{-\left(\frac{1}{(1.38 \times 10^{-23} \text{ J/K})(293.15 \text{ K})}\right) \left(\frac{(6.67 \times 10^{-11} \text{ N m}^2/\text{kg}^2)(5.97 \times 10^{24} \text{ kg})(6.64 \times 10^{-27} \text{ kg})}{(6.371 \times 10^6 \text{ m})}\right)}$$

Wolfram Alpha  $\rightarrow$   $P_{He} = e^{-102.57}$  smaller than N

## ④ Nucleus in a magnetic Field

a) To find the Helmholtz here, let's use the other form  $F = -Nk_B T \ln(z)$ . But we need to know  $z$ , which we can find by plugging in the states of the system.

$$z = \sum_i e^{-\beta E_i} \rightarrow z = (e^{-\beta \epsilon} + e^{-\beta(0)} + e^{-\beta \epsilon})$$

And into Helmholtz.

$$F = -Nk_B T \ln(e^{-\beta \epsilon} + (1) + e^{-\beta \epsilon})$$

$$F = -Nk_B T \ln(2e^{-\beta \epsilon} + 1)$$

b) To find entropy as a function of time, we can use Helmholtz and derive an equation.

$$F = U - TS \rightarrow dF = dU - SdT - TdS$$

Since we can rewrite  $dU = -PdV + TdS$ , we can say

#### ④ Nucleus in a magnetic Field Cont.

$$\delta F = (-P\delta V + T\delta S) - S\delta T - T\delta S$$

$$\delta F = -P\delta V - S\delta T \rightarrow S\delta T = -P\delta V - \delta F$$

$$S = -\frac{P\delta V}{\delta T} - \frac{\delta F}{\delta T} \rightarrow S = -\left(\frac{\partial F}{\partial T}\right)_V$$

Now we can just plug  $F$  from part b into our expression and solve.

$$S = -\frac{\partial}{\partial T} \left( -Nk_B T \ln(2e^{-\beta\epsilon} + 1) \right)$$

Plugging into Wolfram Alpha, and letting  $\beta = \frac{1}{k_B T}$ , we get

$$S = \frac{2N\epsilon e^{-\beta\epsilon}}{T(2e^{-\beta\epsilon} + 1)} + k_B N \ln(2e^{-\beta\epsilon} + 1)$$

#### ④ Nucleus in a magnetic Field Cont.

c) For high temperature,  $\beta$  becomes very small, and our equation tends to a large number. This is consistent with what we know, since we would expect high entropy from a high temperature system.

For low temperature,  $\beta$  becomes very large, and our equation tends toward a small number. Meaning we get a small value for entropy with a low temperature value. Aside from making sense in context with the previous result, it makes sense conceptually. If we have low  $T$ , our system has low Energy and therefore has fewer microstates/ Energy Eigenstates which is what we define low entropy to be. Therefore, it's cool.

## ⑤ Heat Capacity for a Particle in a Box

a)  $E_n = E_1 n^2$  where  $n = 1, 2, 3, \dots$  and  $k_B T \gg E_1$

To Solve for entropy here, we can use Helmholtz, but we need  $Z$  first. Let's solve.

$$Z = \sum_n e^{-\beta E_n} \rightarrow \sum_{n=1,2,3,\dots} e^{-\left(\frac{1}{k_B T}\right)(E_1 n^2)} \rightarrow \int_1^\infty e^{-\frac{E_1 n^2}{k_B T}} dn$$

We can pull a sneaky here and integrate over all space and divide our function by 2 because its Symmetric and integrating  $1 \rightarrow \infty$  is gross.

$$Z = \int_1^\infty e^{-\frac{E_1 n^2}{k_B T}} dn \rightarrow Z = \frac{1}{2} \int_{-\infty}^\infty e^{-\frac{E_1 n^2}{k_B T}} dn$$

$$Z = \frac{\sqrt{\pi}}{4} \left( \frac{1}{\sqrt{\frac{E_1}{k_B T}}} \right) \rightarrow \text{Since } k_B T \gg E_1 \rightarrow \text{we can say } \sqrt{\frac{E_1}{k_B T}} \ll 1$$

Now we plug into Helmholtz.

$$F = -k_B T \ln(Z) = U - TS \rightarrow S = -\left(\frac{\partial F}{\partial T}\right)_V$$

## ⑤ Heat Capacity for a Particle in a Box Cont.

$$S = -\frac{d}{dT} \left( -K_B T \ln \left[ \sqrt{\frac{\pi}{4}} \left( \frac{1}{\sqrt{\frac{E_i}{K_B T}}} \right) \right] \right)$$

$$S = \frac{d}{dT} \left( K_B T \ln \left[ \sqrt{\frac{\pi}{4}} \left( \frac{1}{\sqrt{\frac{E_i}{K_B T}}} \right) \right] \right)$$

$$S = \frac{K_B}{2} \left[ \ln \left( \frac{\sqrt{\frac{\pi}{4}}}{\sqrt{\frac{E_i}{K_B T}}} \right) - 1 \right]$$

b) Now we need to solve for  $C_V$

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

All we need to do is plug in our Entropy expression into the second form of the given formula.

$$C_V = \frac{d}{dT} \left( \frac{K_B}{2} \left[ 1 - \ln \left( \frac{\sqrt{\frac{\pi}{4}}}{\sqrt{\frac{E_i}{K_B T}}} \right) \right] \right) \rightarrow \text{Wolfram} \rightarrow C_V = \frac{K_B}{2}$$