

The Gibbs Factor and The Grand Partition Function

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Roadmap

- 1) Brief Review of Antu's Guest Lecture on the Partition Function
- 2) What Happens When We Exchange Particles? (Derivation of Gibbs Factor)
- 3) Probability of such a system
- 4) Grand Partition Function Derivation
- 5) Multiple Particle Type Case
- 6) A Fun Example

How Did We Get Our Partition Function Before?

- Started with isolated system with energy reservoir (**microcanonical**)
- Used Fundamental Postulate of Stat Mech to say all microstates of energy that fall between E and ΔE are equally probable to occur (**microcanonical**)
- We now set up a system that exchanges energy and has a temperature reservoir
- If energy is exchanged so is entropy so we have non uniform probability distribution

$$P(s) \propto \Omega(s) \quad \text{and} \quad S = k \ln(\Omega) \quad \text{so} \quad \ln(\Omega) = S/k \longrightarrow \Omega = e^{S/k} \quad (1)$$

$$\frac{P(s_2)}{P(s_1)} = \frac{\Omega(s_2)}{\Omega(s_1)} = \frac{e^{S(s_2)/k}}{e^{S(s_1)/k}} = e^{\Delta S/k} \quad (2)$$

$$dS_R = \frac{1}{T} (dU_R + PdV_R - \mu dN_R) \quad (3)$$

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What Happens When We Exchange Particles?

We now have: fundamental thermo identity $dS_R = \frac{1}{T} (dU_R + PdV_R - \mu dN_R)$

Same Principle as with other Partition Function: $PdV \ll dU$, but this time $dN \neq 0$

$$\Delta S_R = - \frac{1}{T} [E(s_2) - E(s_1) - \mu N(s_2) + \mu N(s_1)]$$

$$\frac{P(s_2)}{P(s_1)} = \frac{e^{-[E(s_2) - \mu N(s_2)]/kT}}{e^{-[E(s_1) - \mu N(s_1)]/kT}}$$

$$\text{Gibbs Factor} = e^{-[E(s) - \mu N(s)]/kT}$$

Same Derivation as Partition except we take $N(s)$ into account due to exchange of particles

We use the same logic as before: a ratio of probabilities is equal to a ratio of exponentials

In this way we generalize:
Gibbs Factor is analogous to the Boltzmann Factor

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What is the Probability it's in Given Any State?

$$\text{Gibbs Factor} = e^{-[E(s)-\mu N(s)]/kT}$$

$$\frac{P(s1)}{e^{-[E(s1)-\mu N(s1)]/kT} P(s)} = \frac{P(s2)}{e^{-[E(s2)-\mu N(s2)]/kT} P(s)}$$
$$= \frac{1}{Z}$$
$$P(s) = \frac{1}{Z} e^{-[E(s)-\mu N(s)]/kT}$$

We have our Gibbs factor which we just derived

The argument is that the probability of any given state divided by the Gibbs factor of any state is equal regardless of state. This means that the argument is not dependent on the state and is equal to a proportionality factor which we write as $(1/Z)$.

Rearranging we get the general probability with our constant of proportionality $(1/Z)$

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Grand Partition Function (\mathcal{Z})

$$P(s) = \frac{1}{\mathcal{Z}} e^{-[E(s) - \mu N(s)]/kT}$$

$$\sum_s P(s) = \sum_s \frac{1}{\mathcal{Z}} e^{-[E(s) - \mu N(s)]/kT} = 1$$

$$\mathcal{Z} = \sum_s e^{-[E(s) - \mu N(s)]/kT}$$

We have our previously derived probability for all states

Sum of all probabilities is equal to 1. \mathcal{Z} doesn't depend on E or N so we can rearrange:

Our Grand Partition Function!

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Can This System Scale Based On Different Particles?

What if our system has different types of molecules?

μdN term becomes a sum over species $\mu_i dN_i$

We can modify all of our **Gibbs Factors** accordingly

Ex (2 different types a and b):

Gibbs Factor 2 particles = $e^{-[E(s)-\mu_a N_a(s)-\mu_b N_b(s)]/kT}$

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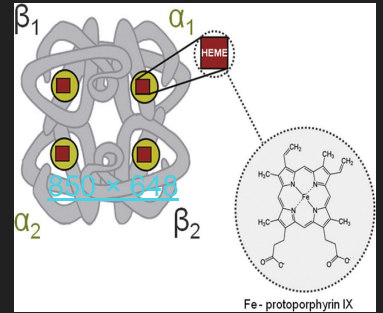
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Biology Application

1. Hemoglobin molecule has 4 absorption sites
2. Each site can carry only one oxygen molecule (O_2)
3. Let's just look at 1 of the sites and treat as independent of others
4. If only one oxygen can bind, we have two states: occupied ($\epsilon = -0.7\text{eV}$ $\mu = \mu$) and unoccupied ($\epsilon = 0\text{ eV}$ $\mu = 0$)

Grand Partition function for single site system:

$$Z = e^{0/kT} + e^{-[\epsilon - \mu]/kT} = 1 + e^{-[\epsilon - \mu]/kT}$$



Application Cont.

1. Chemical potential μ in lungs relatively high (lots of oxygen)
2. Near lungs blood in diffusive equilibrium with atmosphere, partial pressure of oxygen is 0.2 atm
3. Using equation 6.93 from Schroeder which is related to our derivation of μ for an ideal gas, (pg. 255): $\mu = -kT \ln[(VZ_{\text{int}})/(NV_Q)] \approx -0.6 \text{ eV}$ @Body Temp=310K

$$e^{-[\epsilon - \mu]/kT} \approx e^{(0.1 \text{ eV})/kT} \approx 40, \quad \text{So using our probability function: } P(s) = \frac{e^{-[E(s) - \mu N(s)]/kT}}{Z}$$

The probability of any given state being occupied is therefore:

$$P(\text{occupied by O}_2) = \frac{40}{1+40} = 98\% \quad (\text{our lungs are really efficient!!})$$

Different Particles?

1. Say we allow for Carbon Monoxide (CO) to be able to bind to the site
2. Now there are three states available, unoccupied, occupied oxygen ($\epsilon = -0.7\text{eV}$ $\mu = -0.6\text{eV}$), and occupied carbon monoxide ($\epsilon' = -0.85\text{eV}$ $\mu' = -0.72\text{eV}$)

$$Z = e^{0/kT} + e^{-[\epsilon - \mu]/kT} + e^{-[\epsilon' - \mu']/kT}, \text{ where } e^{-[\epsilon' - \mu']/kT} \approx 120$$

$$P(\text{occupied by O}_2) = \frac{40}{1+40+120} = 25\%$$

Probability of the site being occupied by an oxygen molecule drops! This is why carbon monoxide poisoning is deadly!!

Summary and A Look Ahead

1. Grand Partition Function is just the partition function with an exchange of particles
2. **Gibbs Factor** = $e^{-[E(s)-\mu N(s)]/kT}$
3. $P(s) = \frac{1}{Z} e^{-[E(s)-\mu N(s)]/kT}$ (Probability)
4. $Z = \sum_s e^{-[E(s)-\mu N(s)]/kT}$ (Grand Partition)
5. **Gibbs Factor For Multiple Particles** = $e^{-[E(s)-\mu_a N_a(s)-\mu_b N_b(s)]/kT}$

In the same way that the Helmholtz Free Energy could be calculated: $F = -kT \ln(Z)$

The Grand Free Energy could be calculated: $\phi = -kT \ln(Z)$, where Z is the grand partition function!