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6. Gibbs sum for a two level system.

Consider a system that may be unoccupied with energy zero or occupied by one particle in either of two states, one of energy zero and one of energy ε. Show that the Gibbs sum for this system is:

$$\Im = 1 + \lambda + \lambda e^{-\varepsilon/\tau}$$

Our assumption excludes the possibility of one particle in each state at the same time. Notice that we include in the sum a term for N=0 as a particular state of a system of a variable number of particles.

Solution:

The definition of the Gibbs sum is:

$$\Im \equiv \sum_{ASN} e^{\left(N\mu - \varepsilon_{s(N)}\right)/\tau}$$

Where the summation is taken over all states for all numbers of particles. Note the unoccupied state has N=0 and the energy is zero.

$$\Im \equiv \sum_{ASN} e^{\left(N\mu - \varepsilon_{s(N)}\right)/\tau}$$

$$\Im = \sum_{N=0}^{\infty} \sum_{S(N)} e^{\left(N\mu - \varepsilon_{s(N)}\right)/\tau}$$

$$\Im = \sum_{N=0}^{1} e^{(N\mu - \varepsilon_1)/\tau} + e^{(N\mu - \varepsilon_2)/\tau}$$

$$\Im = \sum_{N=0}^{1} e^{(N\mu)/\tau} + e^{(N\mu - \varepsilon)/\tau}$$

$$\Im = e^{(0\mu)/\tau} + e^{(1\mu)/\tau} + e^{(1\mu - \varepsilon)/\tau}$$

$$\Im = 1 + e^{\mu/\tau} + e^{\mu/\tau} e^{-\varepsilon/\tau}$$

$$\lambda \equiv e^{\mu/\tau} \quad \text{absolute activity}$$

$$\Im = 1 + \lambda + \lambda e^{-\varepsilon/\tau}$$

Show that the thermal average occupancy of the system is:

$$\langle N \rangle = \frac{\lambda + \lambda e^{-\varepsilon/\tau}}{\Im}$$

Solution:

By definition, the thermal average number of particles is:

$$\langle N \rangle = \lambda \frac{\partial}{\partial \lambda} \log \Im$$

$$\langle N\rangle = \lambda\frac{\partial}{\partial\lambda}\log\left[1+\lambda+\lambda e^{-\varepsilon/\tau}\right]$$

$$\langle N\rangle = \lambda\frac{1}{\left[1+\lambda+\lambda e^{-\varepsilon/\tau}\right]}\frac{\partial}{\partial\lambda}\left[1+\lambda+\lambda e^{-\varepsilon/\tau}\right]$$

$$\langle N\rangle = \lambda\frac{1}{\left[1+\lambda+\lambda e^{-\varepsilon/\tau}\right]}1+e^{-\varepsilon/\tau}$$

$$\langle N\rangle = \frac{\lambda+\lambda e^{-\varepsilon/\tau}}{\Im}$$

Show that the thermal average occupancy of the state at energy ε is:

$$\langle N(\varepsilon)\rangle = \frac{\lambda e^{-\varepsilon/\tau}}{\Im}$$

Solution:

Start with the absolute probability that the system will be found in state N, ε:

$$\Im \equiv \sum_{ASN} e^{\left(N\mu-\varepsilon_{s(N)}\right)/\tau}$$

$$P(N_1,\varepsilon_1) = \frac{e^{(N_1\mu-\varepsilon_1)/\tau}}{\Im}$$

$$P(N=1,\varepsilon) = \frac{e^{(\mu-\varepsilon)/\tau}}{\Im}$$

$$\langle N(\varepsilon)\rangle = \sum_{ASN} N(\varepsilon)P(N=1,\varepsilon)$$

$$\langle N(\varepsilon)\rangle = \sum_{ASN} N(\varepsilon)\frac{e^{(N_1\mu-\varepsilon_1)/\tau}}{\Im}$$

$$\langle N(\varepsilon)\rangle = \sum_{ASN} N(\varepsilon)\frac{e^{(\mu-\varepsilon)/\tau}}{1+\lambda+\lambda e^{-\varepsilon/\tau}}$$

$$\langle N(\varepsilon)\rangle = \frac{e^{(\mu-\varepsilon)/\tau}}{1+\lambda+\lambda e^{-\varepsilon/\tau}}$$

$$\langle N(\varepsilon)\rangle = \frac{\lambda e^{-\varepsilon/\tau}}{1+\lambda+\lambda e^{-\varepsilon/\tau}}$$

$$\langle N(\varepsilon)\rangle = \frac{\lambda e^{-\varepsilon/\tau}}{\Im}$$

Find an expression for the thermal average energy of the system.

Solution:

Start with the definition of average value and the enumeration that we have N=0 in s=0 and N=1 in s=0,ε.

$$\langle X\rangle=\sum_{ASN}X(N,s)P(N,\varepsilon_s)=\frac{\sum_{ASN}X(N,s)e^{\left(N\mu-\varepsilon_{s(N)}\right)/\tau}}{\Im}$$

$$\langle\varepsilon\rangle=\frac{\varepsilon(N=0,s=0)e^{\left(0\mu-\varepsilon_{s(0)}\right)/\tau}+\varepsilon(N=1,s=0)e^{\left(1\mu-\varepsilon_{s(0)}\right)/\tau}+\varepsilon(N=0,s=1)e^{\left(1\mu-\varepsilon_{s(0)}\right)/\tau}}{\Im}$$

$$\langle\varepsilon\rangle=\frac{0e^{(0\mu-0)/\tau}+0e^{(1\mu-0)/\tau}+\varepsilon e^{(1\mu-\varepsilon)/\tau}}{\Im}$$

$$\langle\varepsilon\rangle=\frac{\varepsilon e^{(\mu-\varepsilon 0)/\tau}}{\Im}$$

$$\langle\varepsilon\rangle=\frac{\varepsilon\lambda e^{-\varepsilon/\tau}}{\Im}$$

Allow the possibility that the orbital at 0 and at ε may be occupied each by one particle at the same time; show that:

$$\Im=1+\lambda+\lambda e^{-\varepsilon/\tau}+\lambda^2e^{-\varepsilon/\tau}=(1+\lambda)\left[1+\lambda e^{-\varepsilon/\tau}\right]$$

Because Z can be factored as shown we have in effect two independent states.

Solution:

$$\Im\equiv\sum_{ASN}e^{\left(N\mu-\varepsilon_{s(N)}\right)/\tau}$$

$$\Im=\sum_{s(N)}e^{\left(0\mu-\varepsilon_{s(0)}\right)/\tau}+\sum_{s(N)}e^{\left(1\mu-\varepsilon_{s(1)}\right)/\tau}$$

$$\Im=e^{\left(0\mu-\varepsilon_{1(0)}\right)/\tau}+e^{\left(1\mu-\varepsilon_{1(1)}\right)/\tau}+e^{\left(1\mu-\varepsilon_{2(1)}\right)/\tau}+e^{\left(1\mu-\varepsilon_{3(1)}\right)/\tau}$$

$$\Im=e^{(0\mu-0)/\tau}+e^{(1\mu-0)/\tau}+e^{(1\mu-\varepsilon)/\tau}+e^{(1\mu-0)/\tau}e^{(1\mu-\varepsilon)/\tau}$$

$$\Im=1+\lambda+\lambda e^{-\varepsilon/\tau}+\lambda^2e^{-\varepsilon/\tau}$$

7. States of positive and negative ionization.

Consider a lattice of fixed hydrogen atoms; suppose that each atom can exist in four states.

State	Number of electrons	Energy
Ground	1	$-\frac{1}{2}\Delta$
Positive Ion	0	$-\frac{1}{2}\delta$
Negative Ion	2	$\frac{1}{2}\delta$
Excited	1	$\frac{1}{2}\Delta$

Find the condition that the average number of electrons per atom be unity. The condition will involve δ, λ, and τ.

Solution: Start with the definitions: $Z \equiv \sum_{N,s(N)} \lambda^N e^{-\varepsilon_{s(N)}/\tau}$ $\langle N \rangle = \lambda \frac{\partial}{\partial \lambda} \log Z$

$$Z \equiv \sum_{N,s(N)} \lambda^N e^{-\varepsilon_{s(N)}/\tau}$$

$$Z = \sum_{s(0)} \lambda^0 e^{-\varepsilon_{s(0)}/\tau} + \sum_{s(1)} \lambda^1 e^{-\varepsilon_{s(1)}/\tau} + \sum_{s(2)} \lambda^2 e^{-\varepsilon_{s(2)}/\tau}$$

$$Z = \lambda^0 e^{\delta/2\tau} + \lambda^1 e^{\Delta/2\tau} + \lambda^1 e^{-\Delta/2\tau} + \lambda^2 e^{-\delta/2\tau}$$

$$Z = e^{\delta/2\tau} + \lambda e^{\Delta/2\tau} + \lambda e^{-\Delta/2\tau} + \lambda^2 e^{-\delta/2\tau}$$

$$\langle N \rangle = \lambda \frac{\partial}{\partial \lambda} \log Z = \frac{\lambda}{Z}\frac{\partial Z}{\partial \lambda} = \frac{\lambda}{Z}\frac{\partial}{\partial \lambda}\left[e^{\delta/2\tau} + \lambda^{1\Delta/2\tau} + \lambda e^{-\Delta/2\tau} + \lambda^2 e^{-\delta/2\tau} \right] = \frac{\lambda}{Z}\left[e^{\Delta/2\tau} + e^{-\Delta/2\tau} + 2\lambda e^{-\delta/2\tau} \right]$$

$$\langle N \rangle = \frac{\lambda\left[e^{\Delta/2\tau} + e^{-\Delta/2\tau} + 2\lambda e^{-\delta/2\tau} \right]}{\left[e^{\delta/2\tau} + \lambda e^{\Delta/2\tau} + \lambda e^{-\Delta/2\tau} + \lambda^2 e^{-\delta/2\tau} \right]}$$

condition where $\langle N \rangle = 1$

$$\langle N \rangle = \frac{\lambda\left[e^{\Delta/2\tau} + e^{-\Delta/2\tau} + 2\lambda e^{-\delta/2\tau} \right]}{\left[e^{\delta/2\tau} + \lambda e^{\Delta/2\tau} + \lambda e^{-\Delta/2\tau} + \lambda^2 e^{-\delta/2\tau} \right]} = 1$$

$$\lambda\left[e^{\Delta/2\tau} + e^{-\Delta/2\tau} + 2\lambda e^{-\delta/2\tau} \right] = \left[e^{\delta/2\tau} + \lambda e^{\Delta/2\tau} + \lambda e^{-\Delta/2\tau} + \lambda^2 e^{-\delta/2\tau} \right]$$

$$e^{\delta/2\tau} + \lambda e^{\Delta/2\tau} + \lambda e^{-\Delta/2\tau} + \lambda^2 e^{-\delta/2\tau} - \lambda e^{\Delta/2\tau} - \lambda e^{-\Delta/2\tau} - 2\lambda^2 e^{-\delta/2\tau} = 0$$

$$e^{\delta/2\tau} - \lambda^2 e^{-\delta/2\tau} = 0$$

$$e^{\delta/2\tau} e^{\delta/2\tau} - \lambda^2 e^{\delta/2\tau} e^{-\delta/2\tau} = 0$$

$$e^{\delta/\tau} - \lambda^2 = 0$$

$$\lambda^2 = e^{\delta/\tau}$$

$\lambda = e^{\delta/2\tau}$ this is the condition for $\langle N \rangle = 1$

8. Carbon monoxide poisoning.

In carbon monoxide poisoning the CO replaces the O2 adsorbed on hemoglobin (Hb) molecules in the blood. To show the effect, consider a model for which each adsorption site on a heme may be vacant or may be occupied either with energy εA by one molecule O2 or with energy εB by one molecule CO. Let N fixed heme sites be in equilibrium with O2 and CO in the gas phases at concentrations such that the activities are $\lambda(O2) = 10^{-5}$ and $\lambda(CO)=10^{-7}$, all at body temperature 37 °C. Neglect any spin multiplicity factors.

First consider the system in the absence of CO. Evaluate εA such that 90 percent of the Hb sites are occupied by O2. Express the answer in eV per O2.

Solution:

The system just has O2 and it can have only energy εA. First express the Gibbs sum:

$$Z \equiv \sum_{ASN} e^{\left(N\mu-\varepsilon_{s(N)}\right)/\tau} = \sum_{N=0}^{\infty}\sum_{S(N)} e^{\left(N\mu-\varepsilon_{s(N)}\right)/\tau} = \sum_{N=0}^{\infty}\sum_{S(N)} \lambda^N e^{-\varepsilon_{s(N)}/\tau}$$

for N=1 $\quad Z_1 = 1+\lambda(O_2)e^{-\varepsilon_A/\tau}$

$$\langle N\rangle = \lambda\frac{\partial}{\partial\lambda}\log Z = \frac{\lambda}{Z}\frac{\partial Z}{\partial\lambda} = \frac{\lambda}{Z}\frac{\partial}{\partial\lambda}\left[1+\lambda(O_2)e^{-\varepsilon_A/\tau}\right] = \frac{\lambda e^{-\varepsilon_A/\tau}}{Z} = \frac{\lambda e^{-\varepsilon_A/\tau}}{1+\lambda(O_2)e^{-\varepsilon_A/\tau}}$$

$$\langle N\rangle = 0.9$$

$$\frac{\lambda e^{-\varepsilon_A/\tau}}{1+\lambda e^{-\varepsilon_A/\tau}} = 0.9 \Rightarrow \lambda e^{-\varepsilon_A/\tau} = 0.9+0.9\lambda e^{-\varepsilon_A/\tau} \Rightarrow .1\lambda e^{-\varepsilon_A/\tau} = 0.9$$

$$\lambda e^{-\varepsilon_A/\tau} = 9$$

activity is $\lambda(O2) = 10^{-5}$ at body temperature 37 °C→310K.

$$\lambda e^{-\varepsilon_A/\tau} = 9$$

$$e^{-\varepsilon_A/\tau} = \frac{9}{\lambda}$$

$$-\varepsilon_A/\tau = \ln\left(\frac{9}{\lambda}\right)$$

$$\varepsilon_A = -\tau\ln\left(\frac{9}{\lambda}\right) = -k_B T\ln\left(\frac{9}{\lambda}\right) = -\left(1.38\cdot10^{-23}JK^{-1}\right)(310K)\ln\left(\frac{9}{10^{-5}}\right)$$

$$\varepsilon_A = -5.6017\cdot10^{-20}J$$

Now admit the CO under the specified conditions. Find εB such that only 10 percent of the Hb sites are occupied by O2.

$$Z \equiv \sum_{ASN} e^{(N\mu - \varepsilon_{s(N)})/\tau} = \sum_{N=0}^{\infty} \sum_{S(N)} e^{(N\mu - \varepsilon_{s(N)})/\tau} = \sum_{N=0}^{\infty} \sum_{S(N)} \lambda^N e^{-\varepsilon_{s(N)}/\tau}$$

for N=1 $\quad Z_1 = 1 + \lambda(O_2)e^{-\varepsilon_A/\tau} + \lambda(CO)e^{-\varepsilon_B/\tau}$

$$\langle N(O_2)\rangle = \lambda(O_2)\frac{\partial}{\partial\lambda(O_2)}\log Z = \frac{\lambda(O_2)}{Z}\frac{\partial Z}{\partial\lambda(O_2)} = \frac{\lambda(O_2)}{Z}\frac{\partial}{\partial\lambda(O_2)}\left[1 + \lambda(O_2)e^{-\varepsilon_A/\tau} + \lambda(CO)e^{-\varepsilon_B/\tau}\right]$$

$$\langle N(O_2)\rangle = \frac{\lambda(O_2)e^{-\varepsilon_A/\tau}}{1 + \lambda(O_2)e^{-\varepsilon_A/\tau} + \lambda(CO)e^{-\varepsilon_B/\tau}} = 0.1$$

$$\lambda(O_2)e^{-\varepsilon_A/\tau} = 0.1\left[1 + \lambda(O_2)e^{-\varepsilon_A/\tau} + \lambda(CO)e^{-\varepsilon_B/\tau}\right]$$

$$\lambda(CO)e^{-\varepsilon_B/\tau} = \lambda(O_2)e^{-\varepsilon_A/\tau} - 0.1\lambda(O_2)e^{-\varepsilon_A/\tau} - 0.1$$

$$e^{-\varepsilon_B/\tau} = \frac{9\lambda(O_2)e^{-\varepsilon_A/\tau} - 1}{\lambda(CO)}$$

$$-\varepsilon_B/\tau = \ln\left(\frac{9\lambda(O_2)e^{-\varepsilon_A/\tau} - 1}{\lambda(CO)}\right)$$

$$\varepsilon_B = -\tau\ln\left(\frac{9\lambda(O_2)e^{-\varepsilon_A/\tau} - 1}{\lambda(CO)}\right) = -k_BT\ln\left(\frac{9\lambda(O_2)e^{-\varepsilon_A/k_BT} - 1}{\lambda(CO)}\right)$$

$$\varepsilon_A = -5.6017\cdot10^{-20}J,\quad k_BT = (1.38\cdot10^{-23}JK^{-1})(310K) = 4.278\cdot10^{-21}J,\quad \lambda(CO) = 10^{-7},\quad \lambda(O_2) = 10^{-5}$$

$$\varepsilon_B = -4.278\cdot10^{-21}J\ln\left(\frac{9\cdot10^{-5}e^{5.6017\cdot10^{-20}J/4.278\cdot10^{-21}J} - 1}{10^{-7}}\right)$$

$$\varepsilon_B = -8.5\cdot10^{-20}J$$

9. Adsorption of O2 in a magnetic field.

Suppose that at most one O2 can be bound to a heme occupied by O2. Consider O2 as having a spin of 1 and a magnetic moment of 1 μB. How strong a magnetic field is needed to change the adsorption by 1 percent at T=300 K? (The Gibbs sum in the limit of zero magnetic field will differ from that of problem 8 because there the spin multiplicity of the bound state was neglected.)

$$Z = 1 + \lambda\left(e^{-(\varepsilon-\mu_B B)/\tau} + e^{-\varepsilon/\tau} + e^{-(\varepsilon+\mu_B B)/\tau}\right) = 1 + \lambda e^{-\varepsilon/\tau}\left(1 + 2\cosh\left(\mu_B B/\tau\right)\right)$$

$\varepsilon =$ energy of occupied site when $B = 0$

when $B = 0$

$$Z = 1 + 3\lambda e^{-\varepsilon/\tau}$$

$$p(O2 \text{ occupied}) = \frac{3\lambda e^{-\varepsilon/\tau}}{1 + 3\lambda e^{-\varepsilon/\tau}} = 0.9$$

$$0.9 + 2.7\lambda e^{-\varepsilon/\tau} = 3\lambda e^{-\varepsilon/\tau}$$

$$\lambda e^{-\varepsilon/\tau} = 0.9/0.3 = 3$$

when $B \neq 0$ change absorption by 1%

$$Z = 1 + \lambda e^{-\varepsilon/\tau}\left(1 + 2\cosh\left(\mu_B B/\tau\right)\right)$$

$$p(O2 \text{ occupied}) = \frac{\lambda e^{-\varepsilon/\tau}\left(1 + 2\cosh\left(\mu_B B/\tau\right)\right)}{1 + \lambda e^{-\varepsilon/\tau}\left(1 + 2\cosh\left(\mu_B B/\tau\right)\right)} = 0.91$$

$$\lambda e^{-\varepsilon/\tau} = 3$$

$$\tau = k_B T = \left(1.38\cdot10^{-23} JK^{-1}\right)\left(300K\right) = 4.278\cdot10^{-21} J,\quad \lambda(CO) = 10^{-7},\quad \lambda(O_2) = 10^{-5}$$

~~$\varepsilon_A = 5.6017\cdot10^{-20} J,\ \varepsilon_A/\tau = 13.094$~~

$$\frac{\lambda e^{-\varepsilon/\tau}\left(1 + 2\cosh\left(\mu_B B/\tau\right)\right)}{1 + \lambda e^{-\varepsilon/\tau}\left(1 + 2\cosh\left(\mu_B B/\tau\right)\right)} = 0.91$$

$$\lambda e^{-\varepsilon/\tau}\left(1 + 2\cosh\left(\mu_B B/\tau\right)\right) = 0.91 + 0.91\lambda e^{-\varepsilon/\tau}\left(1 + 2\cosh\left(\mu_B B/\tau\right)\right)$$

$$0.09\lambda e^{-\varepsilon/\tau}\left(1 + 2\cosh\left(\mu_B B/\tau\right)\right) = 0.91$$

$$\cosh\left(\mu_B B/\tau\right) = \frac{1}{2}\left(\frac{0.91}{0.09\lambda e^{-\varepsilon/\tau}} - 1\right) = \frac{1}{2}\left(\frac{0.91}{0.27} - 1\right) \sim 1.185$$

$$B = \frac{k_B T}{\mu_B}\cosh^{-1}(1.185) = \frac{\cosh^{-1}(1.185)\left(4.278\cdot10^{-21}\text{J}\right)}{9.274\cdot10^{-24}\ \text{JT}^{-1}} \sim 276.44\ \text{T}$$

10. Concentration fluctuations.

The number of particles is not constant in a system in diffusive contact with a reservoir. We have seen that:

$$\langle N \rangle = \frac{\tau}{Z}\left(\frac{\partial Z}{\partial \mu}\right)_{\tau,V}$$

From (59). Show that:

$$\langle N^2 \rangle = \frac{\tau}{Z}\left(\frac{\partial^2 Z}{\partial \mu^2}\right)_{\tau,V}$$

$$\langle N \rangle = \frac{\tau}{Z}\left(\frac{\partial Z}{\partial \mu}\right)_{\tau,V}$$

$$\langle N^2 \rangle = \frac{1}{Z}\sum_{N,S} N^2 e^{(N\mu-\varepsilon_S)/\tau} = \frac{\tau^2}{Z}\sum_{N,S}\frac{\partial^2}{\partial \mu^2} N^2 e^{(N\mu-\varepsilon_S)/\tau} = \frac{\tau^2}{Z}\left(\frac{\partial^2 Z}{\partial \mu^2}\right)_{\tau,V}$$

$$\left\langle (\Delta N)^2 \right\rangle = \left\langle \left(N - \langle N \rangle\right)^2 \right\rangle$$

$$\left\langle (\Delta N)^2 \right\rangle = \langle N^2 \rangle - \langle N \rangle^2$$

$$\left\langle (\Delta N)^2 \right\rangle = \frac{\tau^2}{Z}\left(\frac{\partial^2 Z}{\partial \mu^2}\right)_{\tau,V} - \left(\frac{\tau}{Z}\left(\frac{\partial Z}{\partial \mu}\right)_{\tau,V}\right)^2$$

$$\left\langle (\Delta N)^2 \right\rangle = \tau^2\left(\frac{1}{Z}\left(\frac{\partial^2 Z}{\partial \mu^2}\right) - \frac{1}{Z^2}\left(\frac{\partial Z}{\partial \mu}\right)^2\right)$$

b. Show that this may be written as:

$$\left\langle (\Delta N)^2 \right\rangle = \tau \frac{\partial \langle N \rangle}{\partial \mu}$$

$$\tau \frac{\partial \langle N \rangle}{\partial \mu} = \tau \frac{\partial}{\partial \mu}\left(\frac{\tau}{Z}\left(\frac{\partial Z}{\partial \mu}\right)_{\tau,V}\right) = \tau^2 \frac{1}{Z}\left(\frac{\partial^2 Z}{\partial \mu^2}\right)_{\tau,V} - \tau^2 \frac{1}{Z^2}\left(\frac{\partial Z}{\partial \mu}\right)^2 = \left\langle (\Delta N)^2 \right\rangle$$

$$\therefore \left\langle (\Delta N)^2 \right\rangle = \tau \frac{\partial \langle N \rangle}{\partial \mu}$$