Review

• System in thermal equilibrium with a reservoir at temperature T



• Now use this to calculate thermodynamic properties of more complex systems from microscopic model considerations

Boltzmann Factor

- This is one of the most powerful tools in statistical physics
- Can use it to find the probability of finding the system in any particular microstate, when the system is in thermal equilibrium with a reservoir at temperature T



• Simple system to consider first: single atom + reservoir

Probability

- If the atom was completely isolated from the rest of the Universe
 - Each of the energy levels would be equally probable
 - However, it is not it can exchange energy with some "reservoir" at a fixed temperature T
- In this case, the atom will more than likely be found in some states rather than others
- states rather than others
 Depending on their energies
 Consider two states of the atom: s₁ and s₂ *Consider two states of the atom:* s₁ and s₂
 - Since the system (atom + reservoir) is isolated, so we can say that all possible states for the combined atom + reservoir system are equally probable



Probability

- $\Omega_{R}(s_{1})$ multiplicity of reservoir when atom is in state 1
- $\Omega_R(s_2)$ multiplicity of reservoir when atom is in state 2
- If $\Omega_{R}(s_{1}) = 100$ and $\Omega_{R}(s_{2}) = 50$
 - Then it is twice as probable that the atom will be in \boldsymbol{s}_1 than in \boldsymbol{s}_2
 - Because there are twice as many equally probable states
- The probability is directly proportional to the number of microstates for reservoir



Boltzmann Factor

• Starting from $\frac{P(s_2)}{P(s_1)} = \frac{\Omega_R(s_2)}{\Omega_R(s_1)}$ $S = \frac{e^{S_R(s_2)/k}}{e^{S_R(s_2)/k}} = e^{S_R(s_2) - S_R(s_1)/k}$
dSp====================================
$JS_{R} = \frac{Q_{R}}{T} - S_{R} = \frac{Q_{R}}{T}$ $S_{R}(s_{2}) - S_{R}(s_{1}) = \frac{1}{T} \left[Q_{R}(s_{2}) - Q_{R}(s_{1}) \right]$

 $=\frac{1}{T}\left[E(s_2)-E(s_1)\right]$ plugging backin P(s2) _ p -[E(s2)-E(s,)]/10T = C $= E(s_2)/leT$ = C $= E(s_1)/kT$ Boltzman factor => exp(-E(s)/bT) **Boltzmann Factor**

• Boltzmann factor is proportional to the probability of the corresponding microstate, *s*, with energy *E*(*s*)

 $P(s) \propto e^{-E(s)/kT}$

Total probability of finding the atom in one of the states is 1
 So, to get the probability requires normalization

Partition Function

• The normalization constant is called the partition function: Z

$$Z = \sum_{s} e^{-E(s)/kT}$$

Partition function depends on temperature and thus describes how many states are available

• Now the probability of state, *s*, can be written as $P(s) = \frac{1}{Z} e^{-E(s)/kT}$

This equation is often called the Boltzmann Distribution





held additional quantum num to define our states $N = 1, 2, 3 \dots$ l=0,1,....n-1 look at , state N=2 - 4 states 120,1 Px

Studying Atomic Energy Levels

- To investigate the energy levels of an atom, you need to measure the spectrum
 - Transitions between quantized energy levels
- Can measure the light emitted or absorbed by the atoms



