CLASSICAL STATISTICS

TOPICS COVERED:

➢ Thermodynamic Probability

Thermodynamic probability

- In general, there are many different microstates corresponding to a given macrostate.

- The number of microstates leading to a given macrostate is called the *thermodynamic probability*. It is the number of ways in which a given macrostate can be achieved.

• The thermodynamic probability is an "unnormalized" probability, an integer between one and infinity, rather than a number between zero and one.

- For a kth macrostate, the thermodynamic probability is taken to be ω_k.

- A *true probability* p_k could be obtained as

$$p_k = \frac{\omega_k}{\Omega}$$

where Ω is the *total number of microstates available to the system*.

$$\Omega = \sum_k \omega_k$$

COIN EXAMPLE-DIFFERENCE BETWEEN THERMODYNAMIC PROBABILITY AND ORDINARY PROBABILITY

Macrostate Label	Macrostate		Microstate				ω_k	P_k
k	N_1	N_2	Coin 1	Coin 2	Coin 3	Coin 4		
1	4	0	H	H	H	H	1	1/16
2	3	1	H	H	H	T	4	4/16
			H	H	T	H		
			H	T	H	H		
			T	H	H	H		
3	2	2	H	H	T	T	6	6/16
			H	T	H	T		
			H	T	T	H		
			T	T	H	H		
			T	H	T	H		
			T	H	H	T		
4	1	3	H	T	T	T	4	4/16
			T	H	T	T		
			T	T	H	T		
			T	T	T	H		
5	0	4	T	T	T	T	1	1/16

For N Coins !!!!

$$\omega = \binom{N}{N_1} = \frac{N!}{N_1!(N-N_1)!} \qquad (1)$$

Stirling's Approximation

For $N = 8$ $\qquad \omega_{max} = \dfrac{8!}{4!4!} = 70$

For $N = 1000$ $\qquad \omega_{max} = \dfrac{1000!}{500!500!} = ???$

For such large numbers we can use _Stirling's approximation_: $\qquad \boxed{\ln(n!) \approx n\ln(n) - n}$

$$\omega_{max} = \frac{1000!}{500!500!} \qquad \Rightarrow \qquad \ln(\omega_{max}) = \ln(1000!) - 2\ln(500!)$$

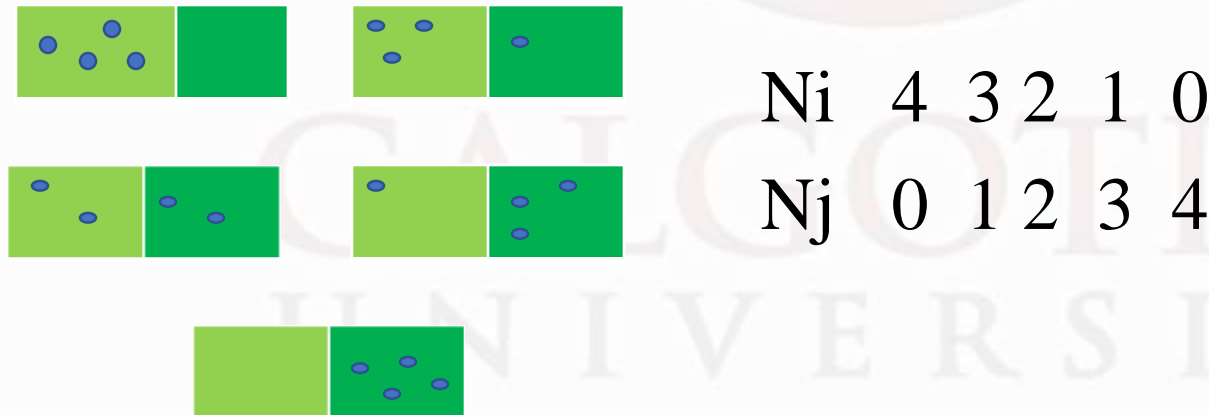$$\ln(\omega_{max}) = \left[1000\ln(1000) - 1000\right] - 2\left[500\ln(500) - 500\right]$$

$$\omega_{max} = 10^{300}$$

Phase Space example- Thermodynamic probability

- Consider two cells in phase space i and j and four phase points or molecules a,b,c and d

- If N_i and N_j are number of phase points or molecules in the cell , then possible macro states are

Ni   4 3 2 1 0

Nj   0 1 2 3 4

- For each of these macro states there will be different micro states

- Consider micro states corresponding to macro state

$$N_i = 3 \text{ and } N_j = 1$$

- There will be four microstates

  Cell i   abc   abd   acd   bcd

  Cell j   d   c   b   a

- Thermodynamic probability for this macro state is w
  = 4

- In general thermodynamic probabilty

  $$w = N!/ n_1!n_2!....n_i!$$

Total number of microstates available to the system having two cells and four particles= 2^4=16

In general= No. of cells ^ No.of particles

Thermodynamic probability and entropy

In classical thermodynamics: as a system proceeds toward a state of equilibrium the entropy increases, and at equilibrium the entropy attains its maximum value

In statistical thermodynamics: system tends to change spontaneously from states with low thermodynamic probability to states with high thermodynamic probability(large number of microstates).

> It was Boltzmann who made the connection between the classical concept of entropy and the thermodynamic probability:
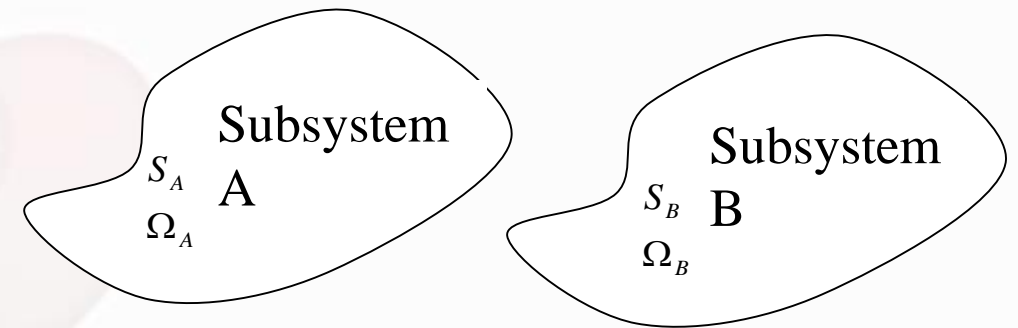>
> $$S = f(\Omega)$$
>
> S and Ω are properties of the state of the system (state variables).

- Consider two subsystems, A and B

$$S_A = f(\Omega_A)$$

$$S_B = f(\Omega_B)$$

Subsystem A
S_A
Ω_A

Subsystem B
S_B
Ω_B

The entropy is an extensive property, it is doubled when the mass or number of particles is doubled.

Consequence: the combined entropy of the two subsystems is simply the sum of the entropies of each subsystem:

$$S_{total} = S_A + S_B \quad or \quad f(\Omega_{total}) = f(\Omega_A) + f(\Omega_B) \quad (3)$$

- One subsystem configuration can be combined with the other to
- give the configuration of the total system. That is,

$$\Omega_{total} = \Omega_A \Omega_B \quad (4)$$

- Example of coin-tossing experiment: suppose that the two
- subsystems each consist of two distinguishable coins.

$$\Omega_{total} = \Omega_A \times \Omega_B = 4 \times 4 = 16$$

Macrostate (N_1 , N_2)	Subsystem A Coin 1	Coin 2	Subsystem B Coin 1	Coin 2	ω_{kA}	ω_{kB}	p_{kA}	p_{kB}
(2 , 0)	H	H	H	H	1	1	1/4	1/4
(1 , 1)	H	T	H	T	2	2	2/4	2/4
	T	H	T	H				
(0 , 2)	T	T	T	T	1	1	1/4	1/4

- Thus Equation (4) holds, and therefore

$$f(\Omega_{total}) = f(\Omega_A \times \Omega_B) \quad (5)$$

Combining Equations (3) and (5), we obtain

$$f(\Omega_A) + f(\Omega_B) = f(\Omega_A \times \Omega_B)$$

The only function for which this statement is true is the logarithm.

Therefore

$$S = k \ln(\Omega)$$

Where k is a constant with the units of entropy. It is, in fact, Boltzmann's constant: $\qquad k = 1.38 \times 10^{-23} J \cdot K^{-1}$

REFERENCES

➢Statistical Mechanics, Satya Prakash

➢A Textbook of Statistical Mechanics, Prof Suresh Chandra, CBS Publishers

➢ Statistical Mechanics, R.K. Pathria, Butterworth Heinemann: 2nd Ed., 1996, Oxford Univers

➢Slide Share

➢Google images