## CHAPTER 12 SEC. 1,2,3,4
STATISTICAL THERMODYNAMICS
INTRODUCTION

Objectives
1. Be able to explain what statistical mechanics is and why it is important.
2. Basic tools of Statistical Mechanics

Introduction to Statistical Mechanics

       Discussion on statistical mechanics (SM) often begins with thermodynamics. Thermal energy (heat) transferred to a molecule does not change the nature of the available energy levels, but it does change which energy levels are occupied by the electrons:
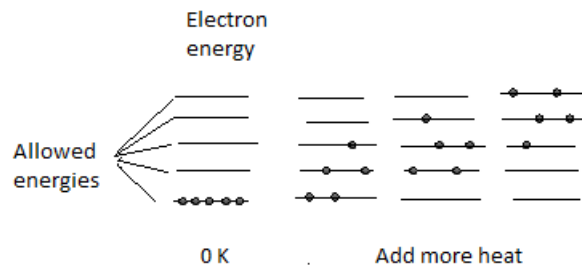
- Within a macroscopic material sample (made up of Avogadro's number of atoms), the total internal energy is still theoretically quantized, though the energy levels may be very close together (so close that we cannot really measure the quantization). At finite temperature, each atom's electrons are excited to some distribution among the available energy levels; with increasing thermal energy in the system, the electrons are able to access higher and higher energy levels. One of the main objectives of statistical mechanics is to predict how the energy levels are occupied for a given model of how a system responds to thermal energy.

- The reason is that SM provides a microscopic basis of thermodynamics and meaning to such terms as entropy and free energy which is otherwise rather hard to understand. Another important reason, not often emphasized enough, is that thermodynamics by itself is not very useful because it does not have the capacity to generate numbers needed to understand experiments. For example, the first two laws define all sorts of relations between thermodynamic variables and functions, but do not tell you how to calculate them. This deficiency partly the reason for the third law which tells that entropy of a perfectly crystalline solid is zero. Remember that this law is used to obtain entropy and enthalpy and then free energy, by integrating temperature dependent specific heat all the way from zero Kelvin.

Q1: What is **Thermodynamics** (TD), **Quantum mechanics** (QM), and **Statistical Mechanics** (SM)?

Thermodynamics deals with the macroscopic properties of matter, e.g. (*P, V, T*). Thermodynamics is not dependent on the fundamental nature of matter. That is, thermodynamics is valid whether matter is made up of atoms and molecules or whether matter is made up of some kind of continuum fabric.

Quantum mechanics deals with the behavior of matter on the microscopic scale. In quantum mechanics we calculate the energy and behavior of a few atoms or small molecules. Most calculations are performed at $T = 0\,\mathrm{K}$. We can't get the macroscopic properties (e.g., the equation of state, etc.) from QM.

☞ Quantum mechanics: stationary state of a system is characterized by a wave function $\psi_N(r_1,...,r_N)$ and energy E_N: microscopic state.

Statistical mechanics is a bridge between quantum mechanics and thermodynamics. We seek to use statistical mechanics to compute macroscopic properties from the quantum mechanical information about the atoms and molecules of interest.

☞ Statistical Physics: Macroscopic state with total energy E, volume V and N particles. Statistical weight $\omega(E,V,N)$ - total number of microstates which correspond to the macrostate E,V,N.

Q2: Why study statistical mechanics?
Consider an example: We have used equations of state (EOS). What are they? They give you a method of calculating one of (*P, V, T*) given any two of them. Usually EOS are cast in some analytic functional form. How do you get EOS?
  I.   Guess some functional form, *P = f (V, T)*. e.g., van der Waals made the guess that
       P=RT/(V-b) – a/V².
 II.   Measure as much *PVT* data as you possibly can *for a specific fluid.*
III.   Regress the parameters in the EOS in some least squares fashion. e.g., find a and b the van der Waals EOS for the fluid.
Do you now have complete information? How about *U, H, S*, etc.?
What happens if you want to find the EOS of a different fluid? For example, you did the above for propane, now you want the EOS for H_2O. In many cases you need to go back to the beginning, i.e., guess a *new* functional form. This is because you can't fit propane and water with the same functional form.
Problems with the above process:
  i.   Very time consuming and very expensive.
 ii.   Have to start all over again for many new fluids.
iii.   Extrapolation outside the region of parameter regression is not valid. Extrapolation often gives unphysical results. For example: What happens in the van der Waals EOS if *V = b*?
 iv.   This process does not give you any physical insight about why the fluid behaves as it does, or how to systematically improve the EOS.
  v.   You don't know anything about many of the other properties.

Is there some way we can get at the EOS from a fundamental approach?
If matter is truly composed of molecules, then it must be the interactions among these molecules that give rise to the macroscopic observable behavior.

Coin-Tossing Model

We assume **the coins are regular and distinguishable** (by a date, or color). This simulates the particles in a lattice, whose location distinguish them. This would be the case for a crystalline solid, as an example. But for other cases, such as molecules in a gas, the particles are identical and indistinguishable and the number of microstates available to the assembly will be correspondingly fewer. We need to develop statistics for both situations.

Lemma I: The number of permutation (the total number of ways in which assignments can be made) of N distinguishable particles is $N!$

Example: For the three balls a, b, c, (3!=6) we have   abc, acb, bca, bac cab, cba.

Lemma II: The number of ways of assigning N distinguishable particles into r distinguishable cells so that there are $N_1,......,N_r$ particles in the respective cells is:

$$\omega = \frac{N!}{\prod_{i=1}^{r} N_i!} \,. \tag{I}$$

Example: For the three balls a, b, c, (3!=6) a, b, c, distributed in two cells with capacity 2 and 1 $3!/(2!1!)=3$ way.

Table 1: two coins

Macrostate Label	Macrostate specification		Microstate		Thermodynamic probability	True Probability	Description
k	N_{1k}	N_{2k}	Coin1	Coin2	$\omega_k = \dfrac{N!}{N_{1k}!N_{2k}!}$	$p_k = \dfrac{\omega_k}{\Omega}$	
1	2	0	H	H	1	$1/4$	Ordered
2	1	1	H T	T H	2	$2/4$	Disordered Or Totally random
3	0	2	T	T	1	$1/4$	Ordered

$$\Omega = \sum_{k=1}^{3} \omega_k = 1+2+1 = 4.$$

$$\omega_{\max} = \frac{N!}{(N/2)!(N/2)!} = \frac{2!}{1!1!} = 2$$

Table 2: Four coins

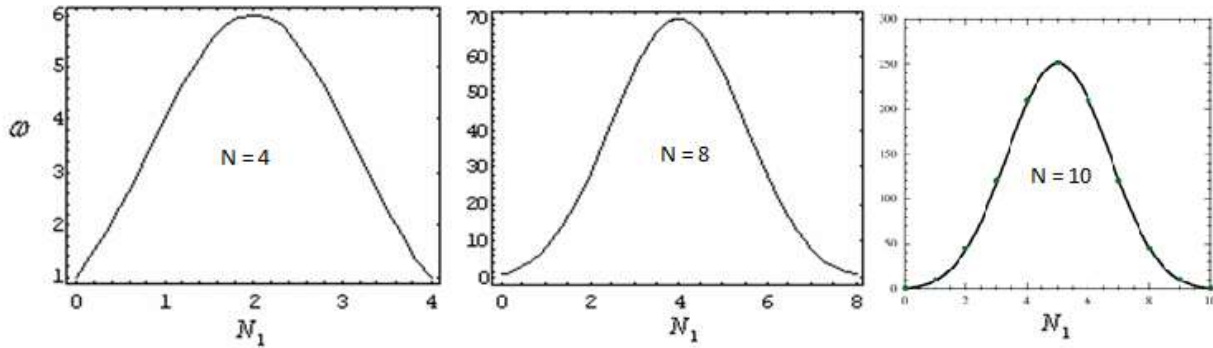| Macrostate Label	Macrostate specification		Microstate				Thermodynamic probability	True Probability	Region
k	N_{1k}	N_{2k}	Coin1	Coin2	Coin3	Coin4	$\omega_k = \dfrac{N!}{N_{1k}!N_{2k}!}$	$p_k = \dfrac{\omega_k}{\Omega}$	
1	4	0	H	H	H	H	1	1/16	Ordered
2	3	1	H	H	H	T	4	4/16	
			H	H	T	H			
			H	T	H	H			
			T	H	H	H			
3	2	2	H	H	T	T	6	6/16	Disordered Or Totally random
			T	T	H	H			
			H	T	H	T			
			T	H	T	H			
			H	T	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	Ordered

$$\Omega = \sum_{k=1}^{5}\omega_k = 1+4+6+4+1 = 16. \qquad (2)$$

$$\overline{N_j} = \frac{\sum_k N_{jk}\omega_k}{\Omega} = \sum_k N_{jk}\frac{\omega_k}{\Omega} = \sum_k N_{jk}P_k \qquad (3)$$

$$\overline{N_1} = \frac{1}{16}\left[(4\times1)+(3\times4)+(2\times6)+(1\times4)+(0\times1)\right] = 2 \qquad \textbf{(4)}$$

$$\overline{N_1}+\overline{N_2} = 4$$

$$\omega_{\max} = \frac{N!}{(N/2)!(N/2)!} = \frac{4!}{2!2!} = 6$$

$$\omega_{\max} = \frac{N!}{(N/2)!(N/2)!} = \frac{10!}{(5)!(5)!} = 252$$

Properties

1- The number of microstates leading to a given macrostate is called the *thermodynamic probability* $"\omega"$. It is the number of ways in which a given configuration can be achieved. This is an "unnormalized" probability, an integer between zero and infinity, rather than a number between zero and one.

2- Multiplicative property

$\omega = \omega_1(E_1, V_1, N_1)\,\omega_2(E_2, V_2, N_2)$

Example: $p_1(N=4) = p_1(N=2)\,p_1(N=2)$.

Example: $\Omega(N=4) = \Omega(N=2)\Omega(N=2) = 2^N$.

3- By increasing the number of coins, the maximum value of the thermodynamic probability $\left(\omega_{max} = \dfrac{N!}{(N/2)!(N/2)}\right)$ increases astronomically.
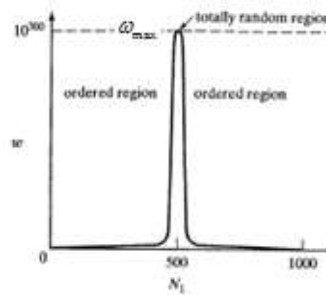

Figure 12.3 Thermodynamic probability versus the number of heads for a coin-tossing experiment with 1000 coins.

4- The "*order region*" almost never occurs; i.e. $\omega \ll \omega_{max}$ compare to the disorder (totally random region) spike, centered with (ω_{max}). The distribution behaves like a $\delta-$function.

5- The total number of microstates is very nearly equal to the maximum number: i.e.

$$\Omega = \sum \omega \approx \omega_{max}$$

6- At w_{max} we can have the particular set $\{N_i\}$, corresponding to the *most probable macrostate*.

7- To calculate the *most probable state,* one has to calculate the slope of the function at the peak and equate it to zero.

8- The most "disordered" macrostate is the state with the highest probability.

9- The macrostate with the highest thermodynamic probability will be the observed equilibrium state of the system.

10- The statistical model suggests that systems tend to change spontaneously from states with low thermodynamic probability to states with high thermodynamic probability.

11- The second law of thermodynamics is a consequence of the theory of probability: the world changes the way it does because it seeks a state of higher probability.

12- The most probable macrostate is the equilibrium state of the assembly. This is the fundamental problem of statistical thermodynamics- to determine the equilibrium state of the system.

**Finally, we are looking for probability density function!!**

We will define the entropy (S) that measure the disorder of the system through the Boltzmann's relation:

$$S = k_B \ln \omega ,$$

where k_B is the Boltzmann's constant and w is the actual number of microstates for a given system.

Way to infer the above expression for the entropy. Problem 12-9

I- Suppose that $S = f(\Omega)$. For a system which consists of two subsystems 1 and 2
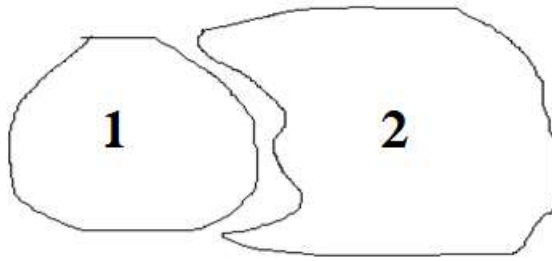
$f(\Omega)$ is a single-valued, monotonically increasing function (because S increases monotonically)

With the following two important properties:

     1- Multiplicative of Ω

$$\Omega_{12} = \Omega_1\Omega_2 \quad \Rightarrow \quad f(\Omega_1\Omega_2) = f(\Omega_1)f(\Omega_2) \qquad\qquad (I)$$

     2- additive (extensive) of S

$$S_{12} = S_1 + S_2 \quad \Rightarrow \quad f(\Omega_1\Omega_2) = f(\Omega_1) + f(\Omega_2) \qquad\qquad (II)$$

Differentiating (II) with respect to Ω_1 (and with respect to Ω_2), we get

$$\Omega_2 f'(\Omega_1\Omega_2) = f'(\Omega_1), \quad \text{and} \quad \Omega_1 f'(\Omega_1\Omega_2) = f'(\Omega_2)$$

So that

$$\Omega_1 f'(\Omega_1) = \Omega_2 f'(\Omega_2) \qquad\qquad (III)$$

Since the left hand side of (III) is independent of Ω_1, and the right hand side is independent of Ω_2, each side must be equal to a constant, independent of both Ω_1 and Ω_2. It follow that $f'(\Omega) = k_B/\Omega$ and hence

$$f(\Omega) = k_B \ln(\Omega) + \text{constant} \qquad\qquad (IV)$$

Substituting from (IV) into (II), we find the constant of integration is zero.

II- Different approach with the help thermodynamics' laws
Physical significant of $\Omega(N, V, E = U)$

(**I**) Consider two systems $A_1(N_1, V_1, E_1)$ and $A_2(N_2, V_2, E_2)$, which are separately in equilibrium and have $\Omega_1(N_1, V_1, E_1)$ and $\Omega_2(N_2, V_2, E_2)$. If the two systems are in contact with the only constrain

$$E = E_1 + E_2 = \text{constant}$$
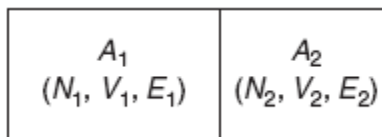
A_1	A_2
$(N_1,\ V_1,\ E_1)$	$(N_2,\ V_2,\ E_2)$

FIGURE 1 Two physical systems being brought into thermal contact.

then

$$\Omega(E_1, E_2) = \Omega_1(E_1)\Omega_2(E_2) = \Omega(E_1, E), \text{ say.}$$

Q1. At what value of E_1 will the composite system in equilibrium?

A1. This will happen at a value $E_1 = \bar{E}_1$, which maximizes the number $\Omega(E_1, E)$.

If $\Omega(E_1, E)$ is maximum, then

$$\left(\frac{\partial \Omega_1}{\partial E_1}\right)_{E_1 = \bar{E}_1} \Omega_2(\bar{E}_2) + \left(\frac{\partial \Omega_2}{\partial E_2}\right)_{E_2 = \bar{E}_2} \Omega_1(\bar{E}_1) \underbrace{\frac{\partial E_2}{\partial E_1}}_{-1} = 0.$$

$$\left(\frac{\partial \ln \Omega_1}{\partial E_1}\right)_{E_1 = \bar{E}_1} = \left(\frac{\partial \ln \Omega_2}{\partial E_2}\right)_{E_2 = \bar{E}_2}$$

(A)

From thermodynamics we know that in such a situation, *thermal equilibrium* is attained when the temperature of the two systems becomes equal, $T_1 = T_2$. In thermodynamics, temperature is defined as

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{V,N}$$

Thus the condition of thermal equilibrium should be

$$\frac{\partial S_1}{\partial E_1} = \frac{\partial S_2}{\partial E_2}$$

(B)

Comparing (A) and (B) we infer

$$S \propto \ln \Omega$$

Since the relation between thermodynamics and statistical mechanics should be fundamental, Boltzmann postulated that the proportionality constant in the above equation should be a universal constant, independent of any particular system. This constant is Boltzmann's constant k_B. Thus we obtain the expression for entropy, which is of central importance in statistical mechanics:

$$S = k_B \ln \Omega$$

(C)

(II) Let us consider there is a transfer of energy ΔE from A_1 to A_2. So, the corresponding change in the entropy of the composite system would be

$$\Delta S = (\Delta S)_{A_1} + (\Delta S)_{A_2} = \Delta E \left[\left(\frac{\partial S_2}{\partial E_2}\right)_{N_2, V_2} - \left(\frac{\partial S_1}{\partial E_1}\right)_{N_1, V_1} \right]$$

According to the second law of thermodynamics, the total entropy S must increase, or at best stay constant, in the transfer process. If ΔE is positive, we must have

$$\left(\frac{\partial S_2}{\partial E_2}\right)_{N_2, V_2} > \left(\frac{\partial S_1}{\partial E_1}\right)_{N_1, V_1} \implies \boxed{T_1 > T_2}$$

Define the following parameters:

$$\zeta = \left(\frac{\partial \ln \Omega(N, V, E)}{\partial N}\right)_{V, E, N = \bar{N}}, \quad \eta = \left(\frac{\partial \ln \Omega(N, V, E)}{\partial V}\right)_{N, E, V = \bar{V}}, \quad \beta = \left(\frac{\partial \ln \Omega(N, V, E)}{\partial E}\right)_{N, V, E = \bar{E}}.$$

where $S = k_B \ln \Omega$. To determine the physical meaning of the parameters η and ζ, we make use of $S = k_B \ln \Omega$ in the equation

$$dS = \left(\frac{\partial S}{\partial E}\right)_{N,V} dE + \left(\frac{\partial S}{\partial V}\right)_{N,E} dV + \left(\frac{\partial S}{\partial N}\right)_{E,V} dN = \beta dE + \eta dV + \zeta dN$$

and the basic formula of thermodynamics, namely

$$dE = TdS - PdV + \mu dN$$

where, P and μ are the thermodynamic pressure and the chemical potential of the system. It follows that

$$\eta = \frac{P}{k_B T}, \qquad \zeta = -\frac{\mu}{k_B T}$$

(**III**) By relaxing one more constrain, i.e. $V = V_1 + V_2 = $ constant , and define

$$\eta = \left(\frac{\partial \ln \Omega}{\partial V}\right)_{V=\bar{V}},$$

one can have $P_1 = P_2$ (*Mechanical equilibrium*) with $T_1 = T_2$.

(**IV**) By relaxing the other constrain, i.e. $N = N_1 + N_2 = $ constant , and define

$$\zeta = \left(\frac{\partial \ln \Omega}{\partial N}\right)_{N=\bar{N}}$$

one can have $\mu_1 = \mu_2$, (*Concentration equilibrium*) with $T_1 = T_2$.

(**V**) Finally, if the exchange is such that all the three (macroscopic) parameters become variable, then the conditions of equilibrium become

$$T_1 = T_2, \quad P_1 = P_2, \quad \text{and} \quad \mu_1 = \mu_2 .$$

Using

$$S(N, V, E) = k \ln \Omega(N, V, E),$$

the intensive parameters, viz. temperature, pressure and chemical potential, are given by

$$\left(\frac{\partial S}{\partial E}\right)_{N,V} = \frac{1}{T}; \quad \left(\frac{\partial S}{\partial V}\right)_{N,E} = \frac{P}{T}; \quad \left(\frac{\partial S}{\partial N}\right)_{V,E} = -\frac{\mu}{T}.$$

Alternatively, we can write

$$P = \left(\frac{\partial S}{\partial V}\right)_{N,E} \bigg/ \left(\frac{\partial S}{\partial E}\right)_{N,V} = -\left(\frac{\partial E}{\partial V}\right)_{N,S}$$

$$\mu = -\left(\frac{\partial S}{\partial N}\right)_{V,E} \bigg/ \left(\frac{\partial S}{\partial E}\right)_{N,V} = \left(\frac{\partial E}{\partial N}\right)_{V,S},$$

$$T = \left(\frac{\partial E}{\partial S}\right)_{N,V}.$$

In deriving these formulae we used the chain rule via

$$\left(\frac{\partial X}{\partial Y}\right)_Z \left(\frac{\partial Y}{\partial Z}\right)_X \left(\frac{\partial Z}{\partial X}\right)_Y = -1.$$

The other thermodynamics functions could be calculated as:

$$\text{Helmoholtz free energy} \quad A(F) \;=\; E(U) - TS$$

$$\text{Gibbs free energy} \quad\quad G \quad\;\; =\; A + PV \;=\; \mu N$$

$$\text{Enthalpy} \quad\quad\quad\quad\; H \quad\;\; =\; E + PV \;=\; G + TS$$

$$C_V = \left(\frac{\partial E}{\partial T}\right)_{N,V} = T\left(\frac{\partial S}{\partial E}\right)_{N,V}$$

$$C_P = \left(\frac{\partial(E + PV)}{\partial T}\right)_{N,P} = T\left(\frac{\partial S}{\partial E}\right)_{N,P} = \left(\frac{\partial H}{\partial T}\right)_{N,P}$$

What are the properties of the entropy?

Answer: The entropy has the following properties:
- 1- The entropy for a simple system is
    - i- continuous,
    - ii- single-valued,
    - iii- differentiable,
    - iv- homogeneous-first-order function of the extensive parameters (N,V,U), and
    - v- Monotone increasing in U.
- 2- The entropy of a composite system is the sum of the entropies of the constituent subsystems: $S(N,V,U) = \sum_i S_i(N_i,V_i,U_i)$.
- 3- The entropy should be maximum at equilibrium.
- 4- The entropy of a simple system approaches zero as $T \to 0$, or $\left(\dfrac{\partial U}{\partial S}\right) \to 0.$

POSTULATE: If we can understand the microscopic interactions we can predict the macroscopic behavior. This is the goal of statistical mechanics. Statistical mechanics relies on determining the most probable distribution of quantum microstates in macroscopic system.

1- For a macroscopic system, define N, V, and U as the Number of particles, volume and the total energy of the system respectively. The *thermodynamics limit* defined as $V \to \infty$ and $N \to \infty$, then the particle density ($v = N/V$) is a fixed quantity at a preassigned value.

2- The microscopic states are defined by two group of parameters
   - a- $\varepsilon_1, \varepsilon_2, ...$ These discrete energies possessed by a single particle, which obtain by solving the wave equation.
   - b- N_1, N_2, …. being the number of particles in this energy state respectively. Hence (for non-interacting particles) we can apply the **constrains**
   $$N = \sum_i N_i ,$$

   and

   $$U = \sum_i N_i \varepsilon_i$$

   where N_i is the number of particles with energy ε_i.

   $$\varepsilon_i \equiv \begin{cases} \text{Classically} \Rightarrow U \ \text{ is contiuous} \\ \text{Quantum} \Rightarrow U \ \text{ is discrete} \end{cases} , \qquad (1)$$

As $\Delta\varepsilon = \varepsilon_i - \varepsilon_j << U$, we might regard U as almost a continuous variable. The specification of the actual values of the macroscopic parameters N, V, and U (i.e. T) then defines a particular *microstate* of the given system.

Notice that: at the molecular level there will be a large numbers of different ways in which the total energy of the system can be distributed among the N particles constituting it. Each of these (different) ways specifies a particular *microstate*, or *complexion*, of the given system.

In conclusion: The whole theory of statistical mechanics is based upon the following postulates:

A-　For each complexion there is a probability "ω" that measure the number of ways in which we can produce it under the conditions:

$$N = \sum_i N_i,$$

and

$$U = \sum_i N_i \varepsilon_i$$

B-　The most probable distribution is that of maximum probability:

$$\frac{\partial \ln \omega}{\partial N_i} = 0$$

C-　Entropy (S) measure the disorder of the system through the relation:

$$S = k_B \ln \omega,$$

where k_B is the Boltzmann's constant and ω is the actual number of microstates for a given system.


Solved examples

Example: Consider an ensemble of $N =18$ distinguishable molecule systems of fixed energy $U = 6\,\varepsilon$ and a fixed volume such that the only individual molecule energy states are fixed as 0, ε, and $2\,\varepsilon$. If N_i is the number of molecules in state i (=0, 1, 2), show by explicit calculation that the full ensemble average and the average in the most probable distribution for (N_i/N) are practically identical.

Solution: With the following constrains:

i-　$N_o + N_1 + N_2 = 18$, and

ii-　$N_o(0) + N_1\varepsilon + N_2(2\varepsilon) = 6\varepsilon$

we have the following distributions:
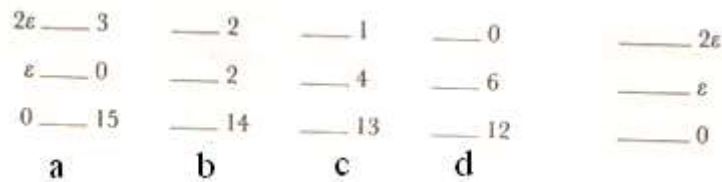
State	Energy (Numbers)	Macrostates			
		a	b	c	d
2	$2\varepsilon(N_2)$	3	2	1	0
1	$\varepsilon(N_1)$	0	2	4	6
0	$0(N_o)$	15	14	13	12
	$\omega_{Macrostates} = N!/\prod_{i=1}^{r} N_i!$	816	18,360	42,840	18,564

With $\Omega = \omega_a + \omega_b + \omega_c + \omega_d = 80,580$

Distribution "c" is the most probable, and even in this few-molecule case, $\ln \Omega = 11.3$ and $\ln \omega_c = 10.7$ do not differ greatly and both are of order $N = 18$. The number of distribution $(M = 4)$ is also of order N.

For the state "c", the most probable distribution is given by:

$$P_o = \frac{N_o}{N} = \frac{13}{18} = 0.722, \quad P_1 = \frac{N_1}{N} = \frac{4}{18} = 0.222, \quad P_2 = \frac{N_2}{N} = \frac{1}{18} = 0.056.$$

The full ensemble average may be calculated as follows: The total number of molecules (Z) in all the replicas of the system is given by: $Z = 18$ $\Omega = 1,450,440$ of which the number in the zero state are:

$$\overline{N_o} = \sum_{i=a}^{d} \omega_i N_{oi} P_i = (816)(15)(1) + (18,360)(14)(1) + (42,840)(13)(1) + (18,564)(12)(1)$$

$$= 1,048,968.$$

The inclusion of the factor ($P_i = 1$) is due to **the equal a priori probability**. The weight factor ω_i differ because of the great difference in the number of micromolecular ways in which these modes of occupation can be realized. Finally,

$$\frac{\overline{N_o}}{Z} = \frac{1,048,968}{1,450,440} = 0.723, \text{ similarly } \frac{\overline{N_1}}{Z} = 0.220, \text{ and } \frac{\overline{N_2}}{Z} = 0.057.$$

These ensemble results agree with the most probable results.

HW 1: Consider an ensemble of $N = 4$ distinguishable molecule systems of fixed energy $U = 12$ ε and a fixed volume such that the only individual molecule energy states are fixed as 1, 2ε, 3 ε, and 4 ε. If N_i is the number of molecules in state i (= 1, 2, 3, 4). Determine the number of possible macrostates and find the number of microstates associated with the macrostates.
Solution: the following constrains:
$N_1 + N_2 + N_3 + N_4 = 4$, and $N_1(\varepsilon) + N_2(2\varepsilon) + N_3(3\varepsilon) + N_4(4\varepsilon) = 12\varepsilon$ have the following distributions:

State	Energy	Macrostates			
		a	b	c	d
3	4ε	2	2	1	0
2	3ε	1	0	2	4
1	2ε	0	2	1	0
0	ε	1	0	0	0
	$\omega_{Macrostates} = N! / \prod_{i=1}^{r} N_i !$	12	6	12	1

HW 2: Consider an ensemble of $N = 4$ distinguishable molecule systems of fixed energy $U = 10$ ε and a fixed volume such that the only individual molecule energy states are fixed as 1, 2ε, 3 ε, and 4 ε . If N_i is the number of molecules in state i (= 1, 2, 3, 4). Determine the number of possible macrostates and find the number of microstates associated with the macrostates.

Solution: the following constrains:
$N_1 + N_2 + N_3 + N_4 = 4$, and $N_1(\varepsilon) + N_2(2\varepsilon) + N_3(3\varepsilon) + N_4(4\varepsilon) = 10\varepsilon$ have the following distributions:

State	Energy	Macrostates				
		a	b	c	d	e
3	4ε	2	1	1	0	0
2	3ε	0	1	0	3	2
1	2ε	0	1	3	0	2
0	ε	2	1	0	1	0
	$\omega_{\text{Macrostates}} = N!/\prod_{i=1}^{r} N_i!$	6	24	4	4	6

HW3: Consider an ensemble of $N = 6$ distinguishable molecule systems of distributed in the energy levels given by the expression:

$$\varepsilon_i = i \times 10^{-20} \text{ Joule}, \qquad i = 0, 1, 2, 3, 4$$

With the total energy

$$U = 4 \times 10^{-20} \text{ J}$$

At room temperature, check the following table:

k	$\{n_0, n_1, n_2, n_3, n_4\}$	ω_k	$S (10^{-23} \text{ JK}^{-1})$	$U (10^{-20} \text{ J})$	$F (10^{-20} \text{ J})$
1	$\{5, 0, 0, 0, 1\}$	6	2.47	4.00	3.26
2	$\{4, 1, 0, 1, 0\}$	30	4.70	4.00	2.60
3	$\{4, 0, 2, 0, 0\}$	15	3.74	4.00	2.89
4	$\{3, 2, 1, 0, 0\}$	60	5.65	4.00	2.32
5	$\{2, 4, 0, 0, 0\}$	15	3.74	4.00	2.89

What is your conclusion?

A- Equal a Priori Probability: *a priori* from the Latin, meaning ``conceived beforehand''. Quantum states that have the same energy have the same probability. To a given macrostate of the system there are in general correspond a large number of microstates, and it seems natural to assume that at any time t the system is equally likely to be in any one of these microstates. The quantity $\omega(N;V;E)$ will be defined as the actual number of possible microstate.