2. Some definitions and assorted mathematical methods

permutations, configurations, system quantum states

boltzons bosons fermions

ensemble average

the most probable distribution

Lagrange multipliers

Stirling's approximation

II. SOME DEFINITIONS and ASSORTED MATHEMATICAL METHODS

- The concept of a distribution and a distribution function:

a distribution – a specification of an entire set of OCCUPATION NUMBERS

Suppose there are a set of states (or boxes),

$1, 2, 3, \cdots i, \cdots$

a sample consisting of N elements (balls or molecules),

each element of the population must be in one of these states (or boxes).

The set of numbers

$N_1 \quad N_2 \quad N_3 \quad \cdots \quad N_i \quad \cdots$ OCCUPATION NUMBERS

which specifies the number of elements (balls or molecules) in each state (or box) is a distribution

[Not all the states need be occupied but every molecule must be assigned to a state]

NUMBER OF DISTRIBUTIONS. If there are a finite number of boxes (g) then the number of ways of putting N objects into g boxes is g^N

Example:

if there are g spin states then the number of ways of putting N spins into g spin states is g^N.

Let $N=3$ $\quad g=2 \quad \alpha$ or β spin states

There are $2^3 = 8$ distributions

Distribution		α	β
1	$\alpha\alpha\alpha$	3	0
2	$\alpha\alpha\beta$	2	1
3	$\alpha\beta\alpha$	2	1
4	$\beta\alpha\alpha$	2	1
5	$\alpha\beta\beta$	1	2
6	$\beta\alpha\beta$	1	2
7	$\beta\beta\alpha$	1	2
8	$\beta\beta\beta$	0	3
		N_1	N_2

OCCUPATION NUMBERS

In other words, we find the number of distributions by counting how many sets of occupation numbers we can get by assigning a state (or box) to each element (or ball).
Can do this only if we have a finite number of states.

- CONSTRAINT

Of course each distribution must satisfy the condition

$$\sum_i N_i = N$$

This condition that must be satisfied is called a constraint

probability of finding any particular element in the state i in the given distribution:

$$P_i = \frac{N_i}{\sum N_i} = \frac{N_i}{N} \qquad \sum_i P_i = 1$$

Example: distribution is $N_1 = 2$, $N_2 = 1$, $N_i = 5$, $N_4 = 1$;

1 2 i 4

If the balls are numbered 1 to 9, the probability of finding ball no. 3 in box i is $5/9$

average: The average of any property G such that G_i be the value of the physical property which the elements of the population have if they are in state i is denoted by $\langle G \rangle$ which is given by

$$\langle G \rangle = \frac{\sum_i N_i G_i}{\sum N_i} = \frac{\sum_i \frac{N_i}{N} G_i}{\sum_i \frac{N_i}{N}} = \frac{\sum_i P_i G_i}{\sum_i P_i}$$

$$= \sum_i P_i G_i = \sum_i \frac{P_i}{\sum_i P_i} G_i$$

normalized distribution function:

$$\frac{P_i}{\sum_i P_i}$$ is a normalized distribution function

$\sum_i P_i$ — normalization of probability

$$= \frac{N_i}{N}$$

Example of spin states

Let G_i be $(I_z)_i = \frac{\hbar}{2}$ in state α or $-\frac{\hbar}{2}$ in state β

average $$\langle I_z \rangle = \sum_{i=\alpha,\beta} \frac{N_i (I_z)_i}{3}$$

For distribution no. 1 $\quad N_1 = 3 \quad N_2 = 0$

$$\langle I_z \rangle = \frac{3(\frac{\hbar}{2})}{3} + \frac{0(-\frac{\hbar}{2})}{3} = \frac{1}{2}\hbar$$

For distribution no. 6 $\quad N_1 = 1 \quad N_2 = 2$

$$\langle I_z \rangle = \frac{1}{3}\left(\frac{\hbar}{2}\right) + \frac{2}{3}\left(-\frac{\hbar}{2}\right) = -\frac{1}{6}\hbar$$

$\langle G \rangle \quad p_i \quad G_i$

Example of 9 harmonic oscillators in 3 vibrational states

one distribution is $\quad N_0 = 5 \quad N_1 = 3 \quad N_2 = 1 \quad N = 9$

o $\quad v = 2 \quad \epsilon_2 = \frac{5}{2}h\nu$

ooo $\quad v = 1 \quad \epsilon_1 = \frac{3}{2}h\nu$

ooooo $\quad v = 0 \quad \epsilon_0 = \frac{1}{2}h\nu$

$$\langle \epsilon \rangle = \frac{5}{9}\left(\frac{1}{2}h\nu\right) + \frac{3}{9}\left(\frac{3}{2}h\nu\right) + \frac{1}{9}\left(\frac{5}{2}h\nu\right)$$
$$= \frac{19}{18}h\nu$$

Some distributions (for example a Boltzmann distribution) have meaning only when a very large number of elements (molecules) are used to populate the states

permutations:

- The number of permutations, that is, the number of ways of placing N distinguishable objects in different orders $= N!$
- The number of ways of assigning N distinguishable objects into r distinguishable containers such that there are $N_1 \; N_2 \cdots N_i \cdots N_r$ objects in the respective boxes

is no. of configurations $= t = \dfrac{N!}{N_1!\,N_2!\cdots N_i!\cdots N_r!}$ for a given distribution

Proof: There are $N_1!$ permutations of objects in the first box and so on. Let the no. of ways of selecting the states for the objects so that occupancy numbers are $N_1, N_2, \cdots$ be t

Total no. of permutations $= t\, N_1!\, N_2! \cdots N_r! = N!$

Example of spins:

No. of ways of assigning 3 spins so that two are in α one in β $= \dfrac{3!}{2!\,1!} = 3$ (that is distributions 2, 3 and 4

number of COMPLEXIONS or COMBINATIONS:

The number of ways of selecting N_1 distinguishable objects from a set of g_1 distinguishable objects is

$$C_{g_1}^{N_1} = \frac{g_1!}{N_1!\,(g_1-N_1)!}$$

also denoted by → $\binom{g_1}{N_1}$

Proof: Divide the g_1 objects into two groups "selected" group of N_1 objects and "not selected" group of (g_1-N_1) objects

distribution $\quad N_1 \quad g_1-N_1 \quad$ total number $= g_1$

occupation numbers

Then $\binom{\text{no. of ways}}{\text{of doing this}} \times N_1!\,(g_1-N_1)! = g_1!$ that is the total no. of permutations.

?

degeneracy

$g_1 = 1 \quad g_2 = 3 \quad g_3 = 2 \quad g_4 = 1$ degeneracy

$N_1 \quad N_2 \quad N_3 \quad N_4$ occupation numbers for the distribution

- Number of ways of selecting N_1 distinguishable objects out of g_1 distinguishable objects $= \dfrac{g_1!}{N_1!(g_1-N_1)!}$

Example:

Let $g_1 = 4$ objects $\underbrace{a\ b\ c\ d}$

$N_1 = 2$ pick two out of four letters

Question: How many possible ways of doing this?

answer: $C_4^2 = \dfrac{4!}{2!(4-2)!}$

All the ways are 12

ab	ba
ca	ac
da	ad
bc	cb
bd	db
cd	dc

Not taking into account the order, the number of ways are 6 $= \dfrac{\text{(all the ways)}}{\text{no. of ways of permuting } N_1 \text{ objects}}$

$$6 = \frac{4!}{(4-2)!\,2!}$$

Example:

An urn contains 3 white balls and 5 black balls. Five balls are drawn at random. What is the probability of drawing 2 white and 3 black balls?

a) No. of ways 2 white balls can be drawn out of 3 white balls (not taking into account the order) is $C_3^2 = \dfrac{3!}{2!(3-2)!}$

b) No. of ways 3 black balls can be drawn out of 5 black balls (not taking into account the order) is $C_5^3 = \dfrac{5!}{3!(5-3)!}$

c) Total No. of ways 5 balls can be drawn out of 8 without regard to color is

$$C_8^5 = \frac{8!}{5!(8-5)!}$$

d) The total no. of ways of drawing 2 white balls and 3 black balls is

$$C_3^2 \cdot C_5^3$$

e) The <u>probability</u> of drawing 2 white balls and 3 black balls if 5 balls are drawn at random =

$$\frac{\text{No. of ways of drawing } 2W+3B}{\text{No. of ways of drawing 5 balls}}$$

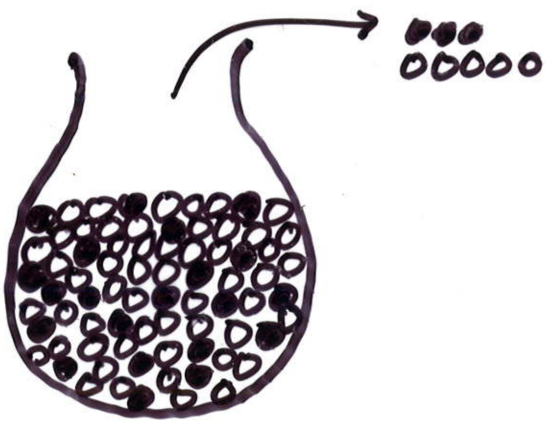
$$= \frac{C_3^2 \cdot C_5^3}{C_8^5} =$$

- What is the probability of drawing K balls n of them black out of an urn with M balls of which N_0 are black?

$$\binom{M}{K} \text{ or } C_M^K = \frac{M!}{K!\,(M-K)!}$$

Answer:

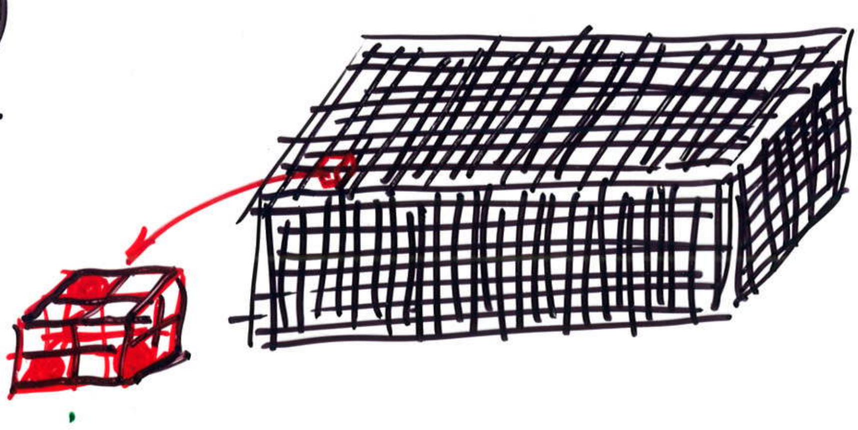
$$P_n = \frac{\binom{N_0}{n}\binom{M-N_0}{K-n}}{\binom{M}{K}}$$



Exactly the same answer as the question

What is the probability of finding a cell with n particles when there are a total of N_0 particles distributed among M sites, given that a site can only be occupied by one particle and that each cell has exactly K sites?

$$P_n = \frac{\binom{N_0}{n}\binom{M-N_0}{K-n}}{\binom{M}{K}}$$



Correspondence is

each black ball represents an occupied site

each white ball represents an empty site

Let both $M \to$ very large and $N_0 \to$ very large

What becomes of P_n?

Let number of cells $= Z$ $\qquad M = KZ$

Let $\langle n \rangle$ be the average occupancy $\qquad N_0 = \langle n \rangle Z$

$$P_n(\langle n \rangle) = \frac{\binom{N_0}{n}\binom{M-N_0}{K-n}}{\binom{M}{K}} = \frac{\binom{\langle n \rangle Z}{n}\binom{(K-\langle n \rangle)Z}{K-n}}{\binom{KZ}{K}}$$

$$= \frac{\dfrac{(\langle n \rangle Z)!}{n!\,(\langle n \rangle Z - n)!}\;\dfrac{[(K-\langle n \rangle)Z]!}{(K-n)!\,((K-\langle n \rangle)Z - K + n)!}}{\dfrac{(KZ)!}{K!\,(KZ-K)!}}$$

Approximation:

$$\frac{N!}{(N-n)!} = \frac{N(N-1)(N-2)(N-3)\cdots\cdots}{(N-n)(N-n-1)(N-n-2)\cdots\cdots} = \underbrace{N(N-1)\cdots(N-n+1)}_{n \text{ terms}}$$

$n \ll N$ so For very large N this is $\approx N^n$

$$\therefore \lim_{Z \to \infty} P_n(\langle n \rangle) = \frac{K!}{n!\,(K-n)!} \cdot \frac{(\langle n \rangle Z)^n\,[(K-\langle n \rangle)Z]^{K-n}}{(KZ)^K}$$

$$= \frac{K!}{n!\,(K-n)!}\;\frac{\langle n \rangle^n (K-\langle n \rangle)^{K-n}}{K^K} \cdot \frac{Z^n Z^{K-n}}{Z^K} \to 1$$

For example:

What is the probability of finding Xe_3 in an alpha cage of zeolite NaA when the average occupancy is 3.5 Xe atoms per cage and there are 8 adsorption sites per cage.

$$P_3(\langle n \rangle = 3.5) = \frac{(3.5)^3 (8-3.5)^5}{8^8} \cdot \frac{8!}{3!\,5!}$$

$$= 0.26408$$

Our approximation applies since $(8 - 3.5)Z$ is very much larger than 8 where $Z \sim 10^{20}$

More general:

$$C_N^{N_1, N_2, N_3, \ldots} = \frac{N!}{N_1!\, N_2!\, N_3! \ldots}$$

is the number of ways of selecting N_1, N_2, N_3, ... distinguishable objects out of a total of N distinguishable objects WITHOUT regard to order

Now consider INDISTINGUISHABLE versus distinguishable and multiple versus single occupancy

Example: 3 distinguishable boxes

$g_1 = 3$

a b c

$N_1 = 2$ 2 distinguishable balls

W B

DISTINGUISHABLE BALLS

Possible ways of arranging:

distribution or arrangement	a	b	c	if INDISTINGUISHABLE BALLS		EXCLUSION if ONLY 1 PER BOX INDISTINGUISHABLE BALLS
1	○	●		1		1
2	○		●	2		2
3		○	●	3		3
4	●	○		(1)		(1)
5	●		○	(2)	duplicates of above	(2)
6		●	○	(3)		(3)
7	○●			4		×
8		○●		5		×
9			○●	6		×
9 distributions				ONLY 6 distributions		ONLY 3 distributions
3^2				$\frac{(3+2-1)!}{2!\,(3-1)!}$		$\frac{3!}{2!\,(3-2)!}$

in general:

$g_i^{N_i}$

$$\frac{(g_i+N_i-1)!}{N_i!\,(g_i-1)!}$$

$$C_{g_i}^{N_i} = \frac{g_i!}{N_i!\,(g_i-N_i)!}$$

How do we find these general expressions?

- Number of ways of putting N_i distinguishable objects into g_i distinguishable boxes is $g_i^{N_i}$ (MB) (if there are NO restrictions as to how many are allowed per box)

For each particle there are g_i possible choices so $g_i^{N_i}$ for N_i particles.

- Number of ways of putting N_i INdistinguishable objects into g_i distinguishable boxes is

$$\frac{(g_i + N_i - 1)!}{N_i!\,(g_i - 1)!}$$

(if there are NO restrictions as to how many are allowed per box) (BE)

Proof: N_i beads on a string $(g_i - 1)$ partitions

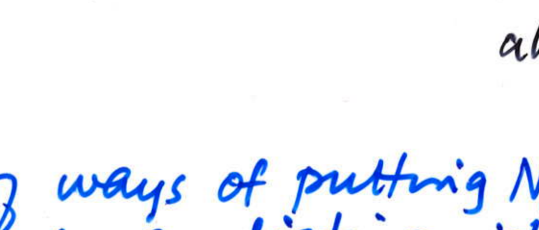
Permute beads $N_i!$
permute partitions $(g_i - 1)!$
allow all permutations
$[N_i + (g_i - 1)]!$

- Number of ways of putting N_i INdistinguishable objects into g_i distinguishable boxes, allowing exactly only one object (or none) per box is

$$C_{g_i}^{N_i} \qquad \frac{g_i!}{N_i!\,(g_i - N_i)!}$$

(FD)

Since an orbital (box) is used only <u>once</u>, classify g_i orbitals into used versus not used



N_i $\qquad$ $g_i - N_i$

Consider a pair of dice, what is the most probable sum?
Answer: That sum which corresponds to the <u>largest number of distinguishable ways</u> Ω of getting it.

Σ	#1	#2	Ω
2	1	1	**1**
3	1	2	**2**
	2	1	
4	1	3	**3**
	2	2	
	3	1	
5	1	4	**4**
	2	3	
	3	2	
	4	1	
6	1	5	**5**
	2	4	
	3	3	
	4	2	
	5	1	
11	5	6	**2**
	5	5	
12	6	6	**1**

Σ	#1	#2	Ω
7	1	6	**6**
	2	5	
	3	4	
	4	3	
	5	2	
	6	1	
8	2	6	**5**
	3	5	
	4	4	
	5	3	
	6	2	
9	3	6	**4**
	4	5	
	5	4	
	6	3	
10	4	6	**3**
	5	5	
	6	4	

What do we mean by the NUMBER OF CONFIGURATIONS t ?

Example: two dice $N = 2$ g = no. of states = 6

Sum =	2	3	4	5	6	7	8	9	10	11	12
no. of configurations t =	1	2	3	4	5	6	5	4	3	2	1

The configurations:

1,1	1,2	1,3	1,4	1,5	1,6	2,6	3,6	4,6	5,6	6,6
	2,1	3,1	4,1	5,1	6,1	6,2	6,3	6,4	6,5	
		2,2	2,3	2,4	2,5	3,5	4,5	5,5		
			3,2	4,2	5,2	5,3	5,4			
				3,3	3,4	4,4				
					4,3					

"system quantum states"

The individual system quantum states have EQUAL A PRIORI probability.

There are 36 configurations in all $g^N = 6^2 = 36$ is the number of distributions

Note that the number of configurations is large for getting 6, 7 or 8 but very small for 2 or 12.

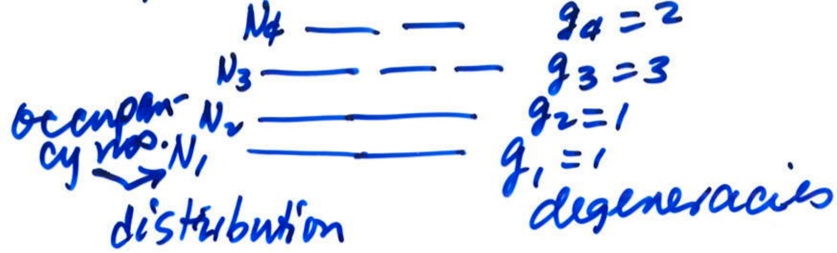
The probability of rolling 7 is $6/36 = 0.1666\ldots$

of rolling 11 is $2/36 = 0.0555\ldots$

The most probable outcome is a 7

Note: The most probable distribution is the one which has a maximum number of configurations.

Given N particles in levels with degeneracies



To find: The total number of configurations

Case A N particles are distinguishable
each level i has degeneracy g_i
⇒ NO restriction as to how many are allowed per box (orbital)
Distribution is N_1 N_2 N_3 ....

$$t = \underbrace{\begin{pmatrix}\text{no. of ways of} \\ \text{assigning } N \\ \text{particles so} \\ \text{there are } N_1, N_2, \ldots \\ \text{in the various} \\ \text{levels}\end{pmatrix}}_{\substack{\text{extra factor due} \\ \text{to DISTINGUISHABILITY} \\ \text{of particles}}} \times \begin{pmatrix}\text{no. of ways of} \\ \text{assigning} \\ N_1 \text{ distinguishable} \\ \text{particles into} \\ g_1 \text{ orbitals}\end{pmatrix} \times \Big(\quad\Big) \times \Big(\quad\Big) \ldots$$

and so on

$$t = \left(\frac{N!}{N_1!\,N_2!\ldots}\right) \times g_1^{N_1} \times g_2^{N_2} \times g_3^{N_3} \ldots$$

BOLTZMANN particles or boltzons
total number of configurations

Case B   N particles are INDISTINGUISHABLE
each level i has degeneracy g_i
⇒ NO restriction as to how many are allowed per orbital
Distribution is N_1 N_2 N_3 . . .

$$t = \begin{pmatrix} \text{no. of ways} \\ \text{of assigning} \\ N_1 \text{ indistinguishable particles} \\ \text{into } g_1 \text{ orbitals} \end{pmatrix} \times \begin{pmatrix} \cdots \\ N_2 \\ \cdots g_2 \end{pmatrix} \times \begin{pmatrix} \cdots \\ \cdots \\ \cdots \end{pmatrix} \times \cdots$$

and so on

$$t = \frac{(g_1 + N_1 - 1)\,!}{N_1\,!\,(g_1 - 1)\,!} \times \frac{g_2 + N_2 - 1}{N_2\,!\,(g_2 - 1)\,!} \times \cdots$$

BOSE-EINSTEIN particles or bosons

Case C   N particles are INDISTINGUISHABLE
each level i has degeneracy g_i
⇒ ONLY ONE particle per orbital
Distribution is N_1 N_2 N_3 . . .

$$t = \begin{pmatrix} \text{no. of ways} \\ \text{of assigning} \\ N_1 \text{ indistinguishable} \\ \text{particles into} \\ g_1 \text{ orbitals} \end{pmatrix} \times \begin{pmatrix} \cdots \\ N_2 \\ g_2 \end{pmatrix} \times \begin{pmatrix} \cdots \end{pmatrix} \times \cdots$$

and so on

all orbitals

$$t = \frac{g_1\,!}{N_1\,!\,(g_1 - N_1)\,!} \times \frac{g_2\,!}{N_2\,!\,(g_2 - N_2)\,!} \times \cdots$$

occupied orbitals

FERMI-DIRAC particles or fermions
total number of configurations

unoccupied orbitals

When the system is small we can actually count the number of configurations

What do we mean by the NUMBER OF CONFIGURATIONS t ?

Example: two dice $N=2$ no. of states $=6=g$

Sum =	2	3	4	5	6	7	8	9	10	11	12
no. of configurations t =	1	2	3	4	5	6	5	4	3	2	1

The configurations:

"system quantum states"	2	3	4	5	6	7	8	9	10	11	12
	1,1	1,2	1,3	1,4	1,5	1,6	2,6	3,6	4,6	5,6	6,6
		2,1	3,1	4,1	5,1	6,1	6,2	6,3	6,4	6,5	
			2,2	2,3	2,4	2,5	3,5	4,5	5,5		
				3,2	4,2	5,2	5,3	5,4			
					3,3	3,4	4,4				
						4,3					

The individual system quantum states have EQUAL A PRIORI probability.

There are 36 configurations in all $g^N = 6^2 = 36$ is the number of distributions

Note that the number of configurations is large for getting 6, 7 or 8 but very small for 2 or 12.

The probability of rolling 7 is $6/36 = 0.1666\ldots$

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The most probable outcome is a 7

Note: The most probable distribution is the one which has a maximum number of configurations.

$\boxed{\text{Now imagine } N \text{ dice where } N \approx 10^{23}}$

What do we do then?

Then it is useful to know what we have found above: THE MOST PROBABLE DISTRIBUTION IS THE ONE WHICH HAS A MAXIMUM NUMBER OF CONFIGURATIONS.

Fundamental assumption of statistical mechanics:

"The properties of an actual equilibrium system are the same as the properties of this most probable distribution"

This is based on the more fundamental assumption that:

"The individual system quantum states have equal a priori probability"

Averages:

ENSEMBLE AVERAGE - Each system is in a particular individual system quantum state. The average over the properties of all systems (an ensemble of systems all having the same number of particles, V and E, for example) is then the average over the properties of all system quantum states with unit weight.

TIME AVERAGE - A particular system in its motion moves through all the possible quantum states of the system consistent with the constraints and spends, on the average, equal time in each. The hypothesis that this is the case is called the ERGODIC hypothesis.

The time average properties of a particular system of N, V, E (for example) are the same as the ENSEMBLE average

Let us now set out to find
the most probable distribution

When we find it, we will calculate its properties.

Then, according to the fundamental assumption of statistical mechanics, these properties (of the most probable distribution) will be THE SAME AS THE PROPERTIES OF AN ACTUAL EQUILIBRIUM SYSTEM.