LECTURE #14

QUANTUM STATISTICAL MECHANICS

AT T=0K, A PHYSICAL SYSTEM OCCUPIES ITS LOWEST ENERGY CONFIGURATION.

AT T > 0K, RANDOM THERMAL ENERGY LEADS TO POPULATION OF EXCITED STATES.

IF WE HAVE A LARGE NUMBER, N, OF PARTICLES IN IN THERMAL EQUILIBRIUM AT TEMPERATURE, T, WHAT IS THE PROBABILITY THAT A GIVEN PARTICLE WILL HAVE A SPECIFIC ENERGY, E_j?

NOTE: THIS PROBABILITY HAS NOTHING TO DO WITH QUANTUM INDETERMINACY ... THE SAME QUESTION ARISES IN CLASSICAL STATISTICAL MECHANICS.

→ WE MUST BE CONTENT WITH A PROBABILISTIC ANSWER BECAUSE WE CANNOT KEEP TRACK OF EACH PARTICLE INDIVIDUALLY (SINCE THERE ARE SO MANY ... e.g., $\sim 10^{23}$ IN A SOLID), WHETHER OR NOT THE UNDERLYING MECHANICS IS DETERMINISTIC.

FUNDAMENTAL ASSUMPTION OF STATISTICAL MECHANICS

IN THERMAL EQUILIBRIUM, EVERY DISTINCT STATE WITH THE SAME TOTAL ENERGY, E, IS EQUALLY PROBABLE.

→ THE TEMPERATURE, T, IS SIMPLY A MEASURE OF THE TOTAL ENERGY FOR A SYSTEM IN THERMAL EQUILIBRIUM

CLASSICALLY, PARTICLES ARE <u>DISTINGUISHABLE</u>.

QUANTUM MECHANICALLY, PARTICLES ARE <u>IDENTICAL</u> AND FALL INTO TWO CLASSES: (1) FERMIONS
(2) BOSONS

→ HOW DO WE COUNT THE DISTINCT STATES IN THESE CASES?

<u>EXAMPLE</u>: THREE NONINTERACTING PARTICLES IN THE 1-D INFINITE SQUARE WELL

$$E = E_A + E_B + E_C = \frac{\pi^2 \hbar^2}{2ma^2}\left(n_A^2 + n_B^2 + n_C^2\right)$$

WHERE $n_A, n_B, n_C = 1, 2, 3, \ldots$

IF $E = 363\left(\frac{\pi^2\hbar^2}{2ma^2}\right) \Rightarrow n_A^2 + n_B^2 + n_C^2 = 363$

$\Rightarrow$ THERE ARE 13 POSSIBILITIES FOR (n_A, n_B, n_C):

(11, 11, 11)

(13, 13, 5), (13, 5, 13), (5, 13, 13)

(1, 1, 19), (1, 19, 1), (19, 1, 1)

(5, 7, 17), (5, 17, 7), (7, 5, 17), (7, 17, 5), (17, 5, 7), (17, 7, 5)

IF THE PARTICLES ARE DISTINGUISHABLE, EACH OF THESE REPRESENTS A DISTINCT QUANTUM STATE THAT IS EQUALLY LIKELY.

WHAT IS THE TOTAL # OF PARTICLES IN EACH STATE? i.e., WHAT IS THE OCCUPATION NUMBER, N_n, FOR STATE ψ_n?

THE COLLECTION OF ALL OCCUPATION NUMBERS FOR A GIVEN THREE PARTICLE STATE IS CALLED THE <u>CONFIGURATION</u>.

IF ALL THREE PARTICLES ARE IN ψ_{11}, THE CONFIGURATION IS:

$$(0,0,0,0,0,0,0,0,0,0,\underset{\uparrow}{3},0,0,\ldots)$$

$N_{11} = 3$, ALL OTHERS ARE ZERO

IF TWO ARE IN ψ_{13} AND ONE IS IN ψ_5, THE CONFIGURATION IS:

$$(0,0,0,0,\underset{\uparrow}{1},0,0,0,0,0,0,0,\underset{\uparrow}{2},0,0,\ldots)$$

$N_5 = 1$ $\qquad$ $N_{13} = 2$, ALL OTHERS ARE ZERO

IF TWO ARE IN ψ_1 AND ONE IS IN ψ_{19}, THE CONFIGURATION IS:

$$(\underset{\uparrow}{2},0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,\underset{\uparrow}{1},0,0,\ldots)$$

$N_1 = 2$ $\qquad$ $N_{19} = 1$, ALL OTHERS ARE ZERO

IF ONE IS IN ψ_5, ONE IS IN ψ_7, AND ONE IS IN ψ_{17}, THE CONFIGURATION IS:

$$(0, 0, 0, 0, 1, 0, 1, 0, 0, 0, 0, 0, 0, 0, 0, 0, 1, 0, 0, \ldots)$$

$N_5 = 1$ $\quad N_7 = 1$ $\quad N_{17} = 1$, ALL OTHERS ARE ZERO

NOTE: CONFIGURATION #4 IS THE MOST PROBABLE (IT CAN BE ACHIEVED IN 6 DIFFERENT WAYS, WHEREAS CONFIGURATIONS #2 AND #3 OCCUR 3 WAYS AND CONFIGURATION #1 OCCURS ONLY 1 WAY)

IF WE SELECT ONE OF THESE PARTICLES AT RANDOM, WHAT IS THE PROBABILITY OF GETTING A SPECIFIC ENERGY E_n?

PROBABILITY OF CONFIGURATION #3 IS $3/13$; WITHIN THIS CONFIGURATION, THERE IS A $2/3$ CHANCE OF E_1 AND A $1/3$ CHANCE OF E_{19}.

$$\therefore P_1 = \frac{3}{13} \times \frac{2}{3} = \frac{2}{13}$$

$$P_{19} = \frac{3}{13} \times \frac{1}{3} = \frac{1}{13}$$

PROBABILITY OF CONFIGURATION #1 IS $1/13$; WITHIN THIS CONFIGURATION, WE ARE CERTAIN TO GET E_{11}.

$$\therefore P_{11} = \frac{1}{13}$$

FOR CONFIGURATION #2, $P_{13} = \frac{3}{13} \times \frac{2}{3} = \frac{2}{13}$

FOR CONFIGURATION #4, $P_7 = P_{17} = \frac{6}{13} \times \frac{1}{3} = \frac{2}{13}$

E_5 EXIST IN CONFIGURATIONS #2 AND #4

$$\therefore \quad P_5 = \frac{3}{13} \times \frac{1}{3} + \frac{6}{13} \times \frac{1}{3} = \frac{3}{13}$$

NOTE: $\sum_{n=1}^{\infty} P_n = P_1 + P_5 + P_7 + P_{11} + P_{13} + P_{17} + P_{19}$
$$= \frac{2}{13} + \frac{3}{13} + \frac{2}{13} + \frac{1}{13} + \frac{2}{13} + \frac{2}{13} + \frac{1}{13} = 1$$

FOR IDENTICAL FERMIONS, PAULI EXCLUSION PRINCIPLE STATES THAT NO TWO PARTICLES CAN OCCUPY THE SAME STATE $\Rightarrow$ CONFIGURATIONS #1, 2, AND 3 ARE NOT ALLOWED

$$\therefore \quad P_5 = P_7 = P_{17} = \frac{1}{3}$$

FOR IDENTICAL BOSONS, THE SYMMETRIZATION REQUIREMENT ALLOWS FOR ONE STATE IN EACH CONFIGURATION.

$$\therefore \quad P_1 = \frac{1}{4} \times \frac{2}{3} = \frac{1}{6}$$
$$P_{19} = \frac{1}{4} \times \frac{1}{3} = \frac{1}{12}$$
$$P_{11} = \frac{1}{4}$$
$$P_{13} = \frac{1}{4} \times \frac{2}{3} = \frac{1}{6}$$
$$P_7 = P_{17} = \frac{1}{4} \times \frac{1}{3} = \frac{1}{12}$$
$$P_5 = \frac{1}{4} \times \frac{1}{3} + \frac{1}{4} \times \frac{1}{3} = \frac{1}{6}$$

NOTE: THE COUNTING OF THE STATES DEPENDS ON THE NATURE OF THE PARTICLES

NOTE: AS N BECOMES A LARGE NUMBER, THE MOST PROBABLE CONFIGURATION BECOMES OVERWHELMINGLY MORE LIKELY

⇒ FOR STATISTICAL PURPOSES, WE CAN AFFORD TO IGNORE OTHER POSSIBILITIES

* THE DISTRIBUTION OF INDIVIDUAL PARTICLE ENERGIES, AT EQUILIBRIUM, IS SIMPLY THEIR DISTRIBUTION IN THE MOST PROBABLE CONFIGURATION.

→ FOR A MORE THOROUGH ANALYSIS OF THIS POINT, SEE KITTEL + KROEMER, THERMAL PHYSICS, Ch. 1.