DRAWING #2: EINSTEIN'S QUANTUM THEORY OF RADIATION I

EINSTEIN'S QUANTUM THEORY OF RADIATION

EINSTEIN (1916) WAS THE FIRST TO PROVIDE INSIGHT INTO THE MECHANISM OF THE EMISSION AND ABSORPTION OF RADIATION.

CONSIDER AN IDEAL GAS OF N ATOMS (OR MOLECULES) IN A VOLUME V IN THERMODYNAMIC EQUILIBRIUM AT TEMPERATURE T (THE CANONICAL ENSEMBLE).

ASSUMING BOHR'S FUNDAMENTAL ASSUMPTION I (THAT AN ATOM CAN ONLY EXIST IN DISCRETE, STATIONARY STATES $\mathcal{E}_1, \mathcal{E}_2, \ldots$ WITH (INTERNAL) ENERGIES $E_1, E_2, \ldots$)

... THEN BY ANALOGY WITH THE BOLTZMANN--GIBBS CANONICAL DISTRIBUTION, WE CAN WRITE FOR THE RELATIVE FREQUENCY $W_n = N_n/N$ (OR PROBABILITY) OF STATE n:

$$W_n = P_n e^{-E_n/k_B T}$$

P_n: "STATISTICAL WEIGHT" OF THE STATE

NOTE; THIS MAY BE SOME WEIGHTING CONSTANT Ω_n (e.g., DEGENERACY) DIVIDED BY THE PARTITION FUNCTION Q;

$$P_n = \frac{\Omega_n}{\sum_j \Omega_j e^{-E_j/k_B T}}$$

k_B: BOLTZMANN CONSTANT

DRAWING #3: EINSTEIN'S QUANTUM THEORY OF RADIATION 2

LET z_n AND z_m BE TWO POSSIBLE STATES OF AN ATOM, SUCH THAT:

- $E_m > E_n$
- THE ATOM IS CAPABLE OF TRANSITIONING FROM z_n TO z_m WITH AN ABSORPTION OF RADIATION $(E_m - E_n)$; SIMILARLY IT CAN EMIT RADIATION BY THE TRANSITION FROM z_m TO z_n (BOHR'S FUNDAMENTAL ASSUMPTION II)

FURTHER LET THE RADIATION ABSORBED OR EMITTED HAVE FREQUENCY ν, WHICH IS CHARACTERISTIC FOR THE (m,n) INDEX COMBINATION.

EMISSION:

A PLANCK OSCILLATOR RADIATES ENERGY WHETHER IT IS EXCITED BY AN EXTERNAL FIELD OR NOT,

... AND SO WITHIN THIS MODEL FOR OUR ATOM, WE CAN ASSUME THAT IT MAY EMIT RADIATION WITHOUT BEING EXCITED BY AN EXTERNAL FIELD.

LET THE PROBABILITY dW THAT THIS WILL HAPPEN DURING A TIME INTERVAL dt BE:

$$dW_e = A_m^n dt$$

A_m^n: CONSTANT, CHARACTERIZING THE PROBABILITY OF THE (m,n) INDEX COMBINATION

$_e$: "EMISSION"

DRAWING #4: EINSTEINS QUANTUM THEORY OF RADIATION 3

ABSORPTION:

IN A RADIATION FIELD, THE ENERGY OF A PLANCK OSCILLATOR IS CHANGED THROUGH THE WORK DONE ON IT BY THE FIELD.

... WHICH CAN BE POSITIVE OR NEGATIVE, DEPENDING ON THE PHASE OF THE OSCILLATOR AND FIELD.

... AND SO WE CAN MAKE THE HYPOTHESES THAT, IN A RADIATION FIELD WITH DENSITY $\rho(\nu)$ OF FREQUENCY ν:

- AN ATOM CAN MAKE A TRANSITION $Z_n \to Z_m$ BY ABSORBING RADIATION OF ENERGY $(E_m - E_n)$ WITH PROBABILITY:

$$dW_{a,f} = B_n^m \rho \, dt$$

B_n^m: CONSTANT, CHARACTERIZING THE PROBABILITY OF THE (n,m) INDEX COMBINATION.

- a,f: "ABSORPTION, FIELD"

- OR IT CAN MAKE THE TRANSITION $Z_m \to Z_n$ BY EMITTING RADIATION OF ENERGY $(E_m - E_n)$ WITH PROBABILITY:

$$dW_{e,f} = B_m^n \rho \, dt$$

- e,f: "EMISSION, FIELD"

IF THE RADIATION IS IN THERMODYNAMIC EQUILIBRIUM WITH THE DISTRIBUTION OF ATOMIC STATES, THEN WE MUST LOOK FOR THE PARTICULAR RADIATION DENSITY FOR WHICH THE EXCHANGE IN ENERGY BETWEEN THE RADIATION AND ATOMS DOES NOT DISTURB THE ATOMIC DISTRIBUTION OF STATES.

THIS CONDITION IS GIVEN BY:

$$\omega_n \, dw_{a,s} = \omega_m dw_e + \omega_m dw_{e,s}$$

$$P_n e^{-E_n/k_BT} B_n^m \rho(\nu) dt = P_m e^{-E_m/k_BT} A_m^n dt + P_m e^{-E_m/k_BT} B_m^n \rho(\nu) dt$$

...WHICH SHOULD HOLD PER UNIT TIME ON AVERAGE; SO:

$$P_n e^{-E_n/k_BT} B_n^m \rho(\nu) = P_m e^{-E_m/k_BT} A_m^n + P_m e^{-E_m/k_BT} B_m^n \rho(\nu)$$

DRAWING #6: EINSTEIN'S QUANTUM THEORY OF RADIATION 5

ASSUMING THAT $\rho(\nu)$ TENDS TO INFINITY WITH T, THIS EXPRESSION REDUCES TO:

$$P_n B_n^m \approx P_m B_m^n$$

THE PRIOR EQUATION THEREFORE BECOMES:

$$P_m e^{-E_n/K_B T} B_m^n \rho(\nu) = P_m e^{-E_m/K_B T} A_m^n + P_m e^{-E_m/K_B T} B_m^n \rho(\nu)$$

THIS EQUATION CAN BE SOLVED FOR $\rho(\nu)$:

$$\rho(\nu) = \frac{A_m^n / B_m^n}{e^{(E_m - E_n)/K_B T} - 1}$$

... WHICH GIVES PLANCK'S LAW AS THE CONDITION FOR THERMODYNAMIC EQUILIBRIUM.

... IF WE ASSOCIATE:

$$E_m - E_n = h\nu$$

... WHICH IS BOHR'S FUNDAMENTAL ASSUMPTION II.

WITH EINSTEIN'S THEORY, WE THEREFORE HAVE A DESCRIPTION OF THE MECHANISM OF ABSORPTION AND EMISSION OF RADIATION...

...IN TERMS OF A GAS OF ATOMS IN THERMODYNAMIC EQUILIBRIUM WITH A RADIATION FIELD.

IN PARTICULAR: THE ATOMS EMIT OR ABSORB RADIATION IN ACCORDANCE WITH THE LAWS OF STATISTICAL MECHANICS...

...WITH TRANSITIONS BETWEEN STATES (m,n) DESCRIBED IN TERMS OF CONSTANTS CHARACTERIZING THE PROBABILITY OF THE (m,n) INDEX COMBINATION.