States of a Model System

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September 12, 2023

- Consider a system of N quantum particles in a stationary quantum state (U, V, N... are independent of time)

- Multiplicity of degeneracy of an energy level ε_n is the number of quantum states, g_n, corresponding to ε_n

- Hydrogen Atom:

    - One proton, one electron
    - $\varepsilon_n = -\dfrac{13.6[\text{eV}]}{n^2}$
    - $\psi_{n,l,m,s} = R_{n,l}(r)\Theta_{l,m}(\theta)\Phi_m(\phi)(s)$
        * n, l, m, s are quantum numbers
        * n is called the principle quantum number
        * l is the angular momentum quantum number
            · $0 \leq l \leq n - 1$
        * m is the magnetic quantum number
            · $-l \leq m \leq l$
        * s is the spin-magnetic quantum number
            · $s = \pm\frac{1}{2}$
        * $g_n = 2n^2$

- Quantum Particle in a Box ($L \times L \times L$)

    - We find $\varepsilon_{n_x,n_y,n_z} = \frac{\hbar^2\pi^2}{2mL^2}(n_x^2 + n_y^2 + n_z^2)$
    - $\psi_{n_x,n_y,n_z}(x,y,z) = \dots$
    - $1 \leq n_x, n_y, n_z \leq \infty$

n_x	n_y	n_z	$\varepsilon_{n_x,n_y,n_z}/A$
1	1	1	3
2	1	1	6
1	2	1	6
1	1	2	6
2	2	1	9
2	1	2	9
1	2	2	9

– We can see that the "6" energy level is degenerate, with a multiplicity of 3, just like "9"

• Binary Model System

  – Energy of the system, $\varepsilon = -MB$

    * M is total magnetic moment: $M = $ (spins up - spins down)$m \rightarrow M = (N_\uparrow - N_\downarrow) m$
    * $(N_\uparrow - N_\downarrow) = 2s$ — spin excess
    * Thus, $\varepsilon = -2mBs$, meaning it is dependent on spin excess
    * $N = 3$ example:
      · $\uparrow\uparrow\uparrow$ — $2s = N_\uparrow - N_\downarrow = 3 \Rightarrow g = 1$
      · $\uparrow\uparrow\downarrow$, $\uparrow\downarrow\uparrow$, $\downarrow\uparrow\uparrow$ — $2s = N_\uparrow - N_\downarrow = 1 \Rightarrow g = 3$
      · $\uparrow\downarrow\downarrow$, $\downarrow\downarrow\uparrow$, $\downarrow\uparrow\downarrow$ — $2s = N_\uparrow - N_\downarrow = -1 \Rightarrow g = 3$
      · $\downarrow\downarrow\downarrow$ — $2s = N_\uparrow - N_\downarrow = -3 \Rightarrow g = 1$
    * In general, there are $N + 1$ values of $2s$ (or M or ε) and 2^N states of the system in total $\Rightarrow$ same energy levels have very high multiplicity

  – Calculation of $g(N, s)$

$$\begin{cases} N_\uparrow - N_\downarrow = 2s \\ N_\uparrow + N_\downarrow = N \end{cases} \qquad \begin{cases} N_\uparrow = \frac{N}{2} + s \\ N_\downarrow = \frac{N}{2} - s \end{cases}$$

  – $g(N, s) = \dfrac{N!}{N_\uparrow! N_\downarrow!}$

  – Drawing from combinatorics below, an approximation of $g(N, s)$ for $N >> 1$ and $s << N$, we can use the Stirling formula:

$$N! \approx \sqrt{2\pi N} \left(\frac{N}{e} \right)^N$$

  – $\ln(N!) \approx N \ln(N) - N + \frac{1}{2}\ln(N) + \frac{1}{2}\ln(2\pi) + 0\left(\frac{1}{N}\right)$
  – $\ln(1 + x) \approx x - \frac{1}{2}x^2 + 0x^3, \quad -1 \leq x \leq 1$
  – Thus, $g(N, s) \approx 2^N \sqrt{\frac{2}{\pi N}} e^{-\frac{2s^2}{N}}$

- Important Combinatorics

  - $(x + y^n) = \sum_{k=0}^{n} \binom{n}{k} x^k y^{n-k}$ — Binomial Expansion

  - $\binom{n}{k} = \frac{n!}{k!(n-k!)}$ — Binomial Coefficient

- Gaussian Probability Density Function (PDF)

$$G(x) = \frac{1}{\sqrt{2\pi}\sigma} e^{-\frac{x^2}{2\sigma^2}}$$

  - σ represents the standard deviation of G

- Macroscopic properties of a large system are well defined (*i.e.* fluctuations about the mean values are small $\approx O(\sqrt{N})$)

- Some Important Definitions:

  - "Closed System" — A system is said to be closed if it has constant energy, U, number of particles, N, volume, V, and other physical properties; a closed system can interact with constant external fields

  - "Accessible Quantum State" — A quantum state is accessible to a system if it is compatible with all physical constraints on the system

  - Fundamental assumption of thermodynamics — A closed system is equally likely to be in any quantum state accessible to it

- Probabilities

  - If the # of accessible quantum states is g, then the probability to find the system in a given state is:

$$P(s) = \begin{cases} 0, & \text{if } s \text{ is not accessible} \\ \dfrac{1}{g}, & \text{if } s \text{ is accessible} \end{cases}$$

  We also know:

$$\underbrace{\sum P(s)}_{\text{all quantum states}} = \underbrace{\sum_{i=1}^{g} \frac{1}{g}}_{\text{accessible only}} = 1$$

  - The average of an observable property of the system, X:

$$\langle X \rangle = \underbrace{\sum X(s)P(s)}_{\text{all quantum } s} = \underbrace{\sum_{i=1}^{g} X(s)\frac{1}{g}}_{\text{accessible } s} = \frac{1}{g}\sum_{i=1}^{g} X(s)$$

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- – $\langle\rangle$ defines the average over all quantum states on ensemble average
  - * An ensemble is a set of replicas of the original system, each replica is in one of the quantum states accessible to the system

$$\boxed{\uparrow\uparrow\downarrow} \quad \boxed{\uparrow\downarrow\uparrow} \quad \boxed{\downarrow\uparrow\uparrow}$$

shows an ensemble of states of a binary model system with $N = 3$, $2s = 1$

- Logarithmic Derivatives

$$\frac{1}{y(x)}\frac{d\,y(x)}{dx} = \frac{d\,\ln(y(x))}{x}$$

  - – The most likely configuration of two binary model systems in thermal contact thus can be found with:

$$\frac{\partial\,\ln(g(N_1, s_1))}{\partial s_1} = \frac{\partial\,\ln(g(N_2, s_2))}{\partial s_2}$$

  - – Using the definition of g from above, we get:

$$\ln\left(2^N\sqrt{\frac{2}{\pi N}}\right)\left(-\frac{2s^2}{N}\right)$$

$$-\frac{4s_1}{N_1} = -\frac{4s_2}{N_2}$$

$$\boxed{\frac{\hat{s}_1}{N_1} = \frac{\hat{s}_2}{N_2}}$$

  - – Using $\hat{s}_1 + \hat{s}_2 = s$, we obtain:

$$\hat{s}_1 + \hat{s}_2 = s \Rightarrow \begin{cases} \hat{s}_1 = \dfrac{sN_1}{N_1 + N_2} \\[2mm] \hat{s}_2 = \dfrac{sN_2}{N_1 + N_2} \end{cases}$$

- How sharp is the maximum $(\hat{s}_1\hat{s}_2)$?

$$\underbrace{g(N_1, \hat{s}_1 + s)g(N_2, \hat{s}_2 - s)}_{\text{\# of q-states in perturbed config}} = \underbrace{g(N_1, \hat{s}_1)g(N_2, \hat{s}_2)e^{-2s^2\left(\frac{1}{N_1} + \frac{1}{N_2}\right)}}_{\text{\# of q-states in most likely config}}$$

  - – Ex. Consider $N_1 = N_2 = 10^{22}$, and $s = 10^{12}$

$$e^{-2s\left(\frac{1}{N_1} + \frac{1}{N_2}\right)} = e^{-400} \approx 10^{-174} <<<< 1$$

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– In summary, the fluctuations of physical properties of large systems about those observed for the most likely configuration are small; average properties of systems in thermal contact are accurately observed by the most likely (thermal equilibrium) configuration