

States of a Model System

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- Consider a system of N quantum particles in a stationary quantum state (U , V , $N \dots$ 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
 - $\varepsilon_n = -\frac{13.6[\text{eV}]}{n^2}$
 - $\psi_{n,l,m,s} = R_{n,l}(r)\Theta_{l,m}(\theta)\Phi_m(\phi)(s)$
 - * 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: $M = (\text{spins up} - \text{spins down})m \rightarrow M = (N_{\uparrow} - N_{\downarrow})m$

- * $(N_{\uparrow} - N_{\downarrow}) = 2s$ — 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 $g(N, s)$

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

- $g(N, s) = \frac{N!}{N_{\uparrow}!N_{\downarrow}!}$

- Drawing from combinatorics below, an approximation of $g(N, s)$ for $N \gg 1$ and $s \ll N$, 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:

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

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 :

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

- $\langle \rangle$ 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

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

- 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:

$$\hat{s}_1 + \hat{s}_2 = s \Rightarrow \begin{cases} \hat{s}_1 = \frac{sN_1}{N_1 + N_2} \\ \hat{s}_2 = \frac{sN_2}{N_1 + N_2} \end{cases}$$

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

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

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

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

- 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
- Thermal equilibrium (most likely) configuration of 2 systems in contact
 - Given two systems, one with N_1 and U_{1o} , and another with N_2 and U_{2o} , the two are put into thermal contact. The energies convert to U_1 and U_2 , respectively. This yields a system with $N_1 + N_2 = N$ and $U_1 + U_2 = U_{1o} + U_{2o} = U$
 - The multiplicity (or number of quantum states) of 1 and 2 combined generates:

$$g(N, U) = \sum_{U_1} g(N_1, U_1) g(N_2, U - U_1)$$

- To find the most likely configuration (U_1), we need to find the largest term of the sum:

$$\begin{aligned} \frac{\partial}{\partial U_1} (g(N_1, U_1) g(N_2, U - U_1)) &\Rightarrow \\ \frac{\partial g(N_1, U_1)}{\partial U_1} g(N_2, U - U_1) + g(N_1, U_1) \frac{\partial g(N_2, U - U_1)}{\partial U_1} (-1) &= 0 \\ \frac{1}{g(N_1, U_1)} \frac{\partial g(N_1, U_1)}{\partial U_1} &= \frac{1}{g(N_2, U_2)} \frac{\partial g(N_2, U_2)}{\partial U_2} \\ \frac{\partial \ln(g(N_1, U_1))}{\partial U_1} &= \frac{\partial \ln(g(N_2, U_2))}{\partial U_2} \end{aligned}$$

- Entropy, σ , is denoted by: $\sigma(N, U) \equiv \ln(g(N, U))$
- Fundamental Temperature, τ , is denoted by: $\frac{1}{\tau} \equiv \frac{\partial \sigma(N, U)}{\partial U} \equiv \left(\frac{\partial \sigma(N, U)}{\partial U} \right)_N$ ¹
- Thus, we can simplify the above to:

$$\frac{1}{\tau_1} = \frac{1}{\tau_2}$$

- When systems 1 and 2, together, are in the most likely configuration, $\tau_1 = \tau_2$, then it is said that 1 + 2 is in thermal equilibrium

$$T = \frac{\tau}{k_B}, \quad \text{Kelvin (absolute) temperature}$$

$$S = k_B \sigma, \quad \text{Conventional entropy}$$

$$k_B = 1.381 \cdot 10^{-23} \left[\frac{\text{J}}{\text{K}} \right], \quad \text{Boltzmann constant}$$

¹The N subscript is used to denote constant, invariable quantities

- Second Law of Thermodynamics (Law of Increase of Entropy):
 - The final entropy will always be greater than or equal to the initial entropy ($\sigma_f \geq \sigma_i$)
 - The entropy of a closed system tends to increase or remain constant when the constraint internal to the system is removed
 - Entropy increase is an irreversible process
- The 0th Law of Thermodynamics:

- If system 1 is in thermal equilibrium with system 3, and 2 is in thermal equilibrium with system 3, then 1 is in thermal equilibrium with 2; that is:

$$\tau_1 = \tau_3 \text{ and } \tau_2 = \tau_3 \Rightarrow \tau_1 = \tau_2$$

- The 1st Law of Thermodynamics:
 - Represents conservation of energy — δQ is the heat added to the system, dU is the change in a system's internal energy, and δW is the work done by the system

$$\delta Q = dU + \delta W$$

- The 2nd Law of Thermodynamics:

- Law of increase of entropy

- The 3rd Law of Thermodynamics:

- As the temperature goes to zero, the entropy goes to a constant (U_g represents the ground state energy)

$$\tau \rightarrow 0 \Rightarrow \sigma \rightarrow C$$

$$\sigma = \ln(g(N, U_g))$$

- Flow of energy for 2 systems in thermal contact

- Given two systems with N_1, U_1 and N_2, U_2 , respectively, we find:

$$\begin{aligned} \sigma &= \sigma_1 + \sigma_2 \\ \Delta\sigma &= \Delta\sigma_1 + \Delta\sigma_2 = \frac{\partial\sigma_1}{\partial U_1} \Delta U_1 + \frac{\partial\sigma_2}{\partial U_2} \Delta U_2 \Rightarrow \\ \frac{1}{\tau_1} \Delta U_1 + \frac{1}{\tau_2} \Delta U_2 &= \frac{1}{\tau_1} (-\Delta U) + \frac{1}{\tau_2} \Delta U \Rightarrow \\ \Delta U \left(\frac{1}{\tau_2} - \frac{1}{\tau_1} \right) &\geq 0 \end{aligned}$$

- * Thus, we expect $\tau_1 \geq \tau_2 \Rightarrow \Delta U \geq 0$
- Energy flows from hot (high energy) to cold (low energy)