Quantum Statistical Mechanics

Nicholas C. Jira, Kenneth Roffo

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Statistical Assumptions

- Any system in thermal equilibrium, every distinct state with energy E is equally probable
  - Fundamental Assumption of Statistical Mechanics
- Thermal motions are random and energy is constantly transfered from one particle to another
  - Conservation of Energy
  - It is *assumed* that no state is prefered
- Quatum mechanics is only interested only in counting distinct states.

3 Particle System

- Take 3 particles in thermal equailibrium
- Three Seperate Energies:

$$\begin{aligned} E &= E_A + E_B + E_C \qquad (1) \\ &= \frac{\pi^2 \hbar^2}{2ma^2}\left(n_A^2 + n_B^2 + n_C^2\right) \end{aligned}$$

- Say, for an example:

$$\begin{aligned} E = 363\left(\frac{\pi^2 \hbar^2}{2ma^2}\right) \qquad (2) \\ n_A^2 + n_B^2 + n_C^2 = 363 \end{aligned}$$

3 Particle System

- Because every quantum state is equally likely, $n_A^2 + n_B^2 + n_C^2$ could be any of the following:

$$(11, 11, 11)$$

$$(13, 13, 5), \quad (13, 5, 13), \quad (5, 13, 13)$$

$$(19, 1, 1), \quad (1, 19, 1), \quad (1, 1, 19)$$

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

3 Particle System

- If each particle is distinguishable, then each represents a specific quantum state
- As long as the system is in thermal equqilibrium, the probability each of these occuring is equal.
- Only care about the total number of particles in each state for ψ_n.
  - The Occupation Number, N_n
- This is done through its configuration

Configuration

- For ψ_{11}:

$$(0,0,0,0,0,0,0,0,0,0,3,0,0,0,0,0,0,0,0,0,...) \tag{3}$$

- For ψ_{13} and ψ_5:

$$(0,0,0,0,1,0,0,0,0,0,0,0,2,0,0,0,0,0,0,0,...) \tag{4}$$

- For ψ_1 and ψ_{19}:

$$(2,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,1,0,...) \tag{5}$$

- For ψ_5, ψ_7 and ψ_{17}

$$(0,0,0,0,1,0,1,0,0,0,0,0,0,0,0,0,1,0,0,0,...) \tag{6}$$

Probability of Distinguishable Particles

- Probability of E_1 is:

$$P_1 = \frac{3}{13} \times \frac{2}{3} = \frac{2}{13} \tag{7}$$

- Probability of E_5 is:

$$P_5 = \left(\frac{3}{13} \times \frac{1}{3}\right) + \left(\frac{6}{13} \times \frac{1}{3}\right) = \frac{3}{13} \tag{8}$$

- This can be done for each individual ψ_n
- The total sum probability for all possibilities would be:

$$P_1 + P_5 + P_7 + P_{11} + P_{13} + P_{17} + P_{19} = 1 \tag{9}$$

Probability of Fermions

- For identical fermion particles, any configuration with more than one occupation number cannot occur.
- Therefore, for this example, only the last configuration is used.
- So the probability of each occuring is:

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

Probability of Bosons

- For identical bosons, symmetry is required
- Therefore, only one state of each cnofiguration is allowed

$$P_1 = \frac{1}{4} \times \frac{2}{3} = \frac{1}{6}$$

$$P_5 = \left(\frac{1}{4} \times \frac{1}{3}\right) + \left(\frac{1}{4} \times \frac{1}{3}\right) = \frac{1}{6} \tag{10}$$

- Once agian, the total probability should be 1

Example Conclusion

- Shows how to count the states of particles
- And how the type of particle affects how the counting occurs
- Based on the probabilities, we see that the particle energies occurs at the most probable configurations

The General Case

- Consider the following system:
  - Arbitrary potentials
  - E_n particle energies
  - d_n degeneracies
  - N_n particles
- Have N_n particles with energy E_n and d_n degeneracies
- We want to know how many distinct states correspond with this configuration.

The General Case - The First Bin

- Start with distinguishable particles in N_1
- Total possibilities are given by the binomial coefficient:

$$\binom{N}{N_1} \equiv \frac{N!}{N_1!(N-N_!)!} \tag{11}$$

- Each time an N is chosen, there is one less N to choose next. Therefore:

$$N(N-1)(N-2)...(N-N_1+1) = \frac{N!}{(N-N_1)!} \tag{12}$$

Within the First Bin

- Look at the total number of ways the N_1 particles could be chosen
- Need to take into account degeneracy, d_1
  - In total - $(d_1)^{N_1}$ possibilities
- So the overall ways to organize the particles within N_1 is:

$$\frac{N! d_1^{N_1}}{N_1!(N - N_1)!} \tag{13}$$

- For N_2 there are only $(N - N_1)$ particles to work with so:

$$\frac{(N - N_1)! d_2^{N_1}}{N_2!(N - N_1 - N_2)!} \tag{14}$$

$Q(N_1, N_2, N_3, ...)$

- In general:

$$
\begin{aligned}
&Q(N_1, N_2, N_3, ...) \qquad (15)\\
&= \frac{N!d_1^{N_1}}{N_1!(N-N_1)!}\frac{(N-N_1)!d_2^{N_1}}{N_2!(N-N_1-N_2)!}\frac{(N-N_1-N_2)!d_3^{N_3}}{N_3!(N-N_1-N_2-N_3)!}...\\
&= N!\frac{d_1^{N_1}d_2^{N_2}d_3^{N_3}\ldots}{N_1!N_2!N_3!...}\\
&= N!\prod_{n=1}^{\infty}\frac{d_n^{N_n}}{N_n!}
\end{aligned}
$$

General Case for Identical Fermoins

- The antisymmetrization requirement for fermions simplifies the case
  - It doesn't matter which particles are in which state
- Also only one particle can occupy each state
- Therefore the total number of ways to choose N_n states are:

$$\binom{d_n}{N_n} \tag{16}$$

- And:

$$Q(N_1, N_2, N_3, ...) = \prod_{n=1}^{\infty} \frac{d_n!}{N_n!(d_n - N_n)!} \tag{17}$$

General Case for Identical Bosons

- Identical Bosons need to take into account symmetry requirements
  - One N-state for each configuration
  - Particles can have the same state
- How many ways can N_n particles be inserted into d_n?
- For $d_n = 5$ and $N_n = 7$

$$\bullet \bullet \times \bullet \times \bullet \bullet \bullet \times \bullet \times \tag{18}$$

  - 7 equivalent particles
  - $d_n - 1$ groups
  - $(N_n + d_n - 1)!$ arrangements

General Case for Identical Bosons

- The number of unique arrangements of N_n into d_n groups is:

$$\frac{(N_n + d_n - 1)!}{N_n!(d_n - 1)!} = \binom{N_n + d_n - 1}{N_n} \tag{19}$$

- And so:

$$Q(N_1, N_2, N_3, ...) = \prod_{n=1}^{\infty} \frac{(N_n + d_n - 1)!}{N_n!(d_n - 1)!} \tag{20}$$

The Most Probable Configuration

- Every state with a given energy and particle number is equally probable
- The most probable state is then the one which occurrs in the largest number of different ways
- This configuration maximizes $Q(N_1, N_2, N_3, ...)$ with constraints:

$$\sum_{n=1}^{\infty} N_n = N$$

$$\sum_{n=1}^{\infty} N_n E_n = E$$

Lagrange Multipliers

- We use Lagrange multipliers for the maximization of Q
- We define

$$G(x_1, x_2, ..., \lambda_1, \lambda_2, ...) \equiv F + \lambda_1 f_1 + \lambda_2 f_2 + ...$$

- We also set all partial derivatives equal to 0

$$\frac{\partial G}{\partial x_n} = 0 \qquad \frac{\partial G}{\partial \lambda_n} = 0$$

- We will use the logarithm, which will turn products into sums.
- Since the logarithm is monotonic, the maxima of Q will occur at the same point as $\ln(Q)$

$$G \equiv \ln(Q) + \alpha \left[N - \sum_{n=1}^{\infty} N_n \right] + \beta \left[E - \sum_{n=1}^{\infty} N_n E_n \right]$$

Distinguishable Particles

$$G \equiv \ln(Q) + \alpha \left[N - \sum_{n=1}^{\infty} N_n \right] + \beta \left[E - \sum_{n=1}^{\infty} N_n E_n \right]$$

- α and β are the Lagrange multipliers, and setting the partial derivatives with respect to these equal to 0 simply returns the constraints.
- We must set the partial derivative with respect to N_n equal to 0.
- If the particles are distinguishable, then we have

$$G = \ln(N!) + \sum_{n=1}^{\infty} [N_n \ln(d_n) - \ln(N_n!)] + \alpha \left[N - \sum_{n=1}^{\infty} N_n \right]$$
$$+\beta \left[E - \sum_{n=1}^{\infty} N_n E_n \right]$$

Distinguishable Particles

- Assuming occupation numbers are large, we may use Stirling's Approximation which states:

$$\ln(z!) \approx z\ln(z) - z \text{for all} z \geq 1$$

- Now G can be rewritten

$$G \approx \sum_{n=1}^{\infty}[N_n \ln(d_n) - N_n \ln(N_n) + N_n - \alpha N_n - \beta E_n N_n]$$
$$+ \ln(N!) + \alpha N + \beta E$$

- Then we have:

$$\frac{\partial G}{\partial N_n} = \ln(d_n) - \ln(N_n) - \alpha - \beta E_n$$

- and solving for the critical points:

$$N_n = d_n e^{-(\alpha + \beta E_n)}$$

Identical Fermions

- For Identical Fermions, we have

$$G = \sum_{n=1}^{\infty} \{\ln(d_n!) - \ln(N_n!) - \ln[(d_n - N_n)!]\} + \alpha \left[N - \sum_{n=1}^{\infty} N_n \right] + \beta \left[E - \sum_{n=1}^{\infty} N_n E_n \right]$$

- Now we must assume not only that N_n is large, but $d_n \gg N_n$
- Applying Stirling's approximation then setting the partial derivative equal to 0 we have

$$N_n = \frac{d_n}{e^{\alpha + \beta E_n} + 1}$$

- the most probable occupation numbers for identical fermions.

Identical Bosons

- For Identical Bosons we have

$$G = \sum_{n=1}^{\infty} \{ \ln[(N_n + d_n - 1)!] - \ln(N_n!) - \ln[(d_n - 1)!] \} + \alpha \left[N - \sum_{n=1}^{\infty} N \right.$$

$$+ \beta \left[E - \sum_{n=1}^{\infty} N_n E_n \right]$$

- Assuming $N_n \gg 1$ and applying Stirling's Approximation we have

$$N_n = \frac{d_n - 1}{e^{\alpha + \beta E_n} - 1}$$

- α is often replaced by the chemical potential

$$\mu(T) = -\alpha k_B T$$

- Here k_B is the Boltzmann constant and T is temperature.
- Plugging this in to our three most probable states equations we have

$$(\epsilon) = \begin{cases} e^{-(\epsilon-\mu)/(k_B T)} & : \text{Maxwell-Boltzmann} \\ \frac{1}{e^{(\epsilon-\mu)/k_B T}+1} & : \text{Fermi-Dirac} \\ \frac{1}{e^{(\epsilon-\mu)/k_B T oys}-1} & : \text{Bose-Einstein} \end{cases}$$

- These distributions are for:
  - Distinguishable Particles - Maxwell-Boltzmann
  - Identical Fermions - Fermi-Dirac
  - Identical Bosons - Bose-Einstein

Photons

- Classified as identical bosons
- Spin 1
- Massless
- Relativistic
- Apply nonrelatavistic assertions about photons

1. $E = h\nu = \hbar\omega$
2. $k = \frac{2\pi}{\lambda} = \frac{\omega}{c}$
3. The only possible spin states are $m = 1, -1$
4. The number of photons rise when the temperature rises.
    - The number of photos is not conserved

Photons

- The total N constraint doesn't apply anymore
- $\alpha = 0$ for the most probable N_n

$$N_\omega = \frac{d_k}{e^{\hbar\omega/k_B T} - 1} \tag{21}$$

- d_k becomes

$$d_k = \frac{V}{\pi^2 c^3}\omega^2 d\omega \tag{22}$$

- Due to $m = -1, 1$ and expressing k in terms of ω

Blackbody Spectrum

- The energy density in $d\omega$ is:

$$\frac{N_\omega \hbar\omega}{V} \tag{23}$$

- and becomes:

$$\rho(\omega) = \frac{\hbar\omega^3}{\pi^2 c^3 \left(e^{\hbar\omega/k_B T - 1}\right)} \tag{24}$$

- Energy per unit volume per unit frequency for an electromagnetic field in thermal equilibrium

Thank You