Lecture 8 - Quantum Distribution Functions

Last time, derived formulas for $Q(N_1, N_2, \dots)$

= # of ways to make configuration $\{N_1, N_2, \dots\}$
= N_n particles with energy E_n

Distinguishable: $Q = N! \prod_{n=1}^{\infty} \frac{d_n^{N_n}}{N_n!}$

Fermions: $Q = \prod \frac{d_n!}{N_n!(d_n - N_n)!}$

Bosons: $Q = \prod \frac{(N_n + d_n - 1)!}{N_n!(d_n - 1)!}$

Today use these to get state of system

Basic plan:
Assume N is really big $\sim 10^{23}$
Then Q's are humongous!

Also turns out that Q is pretty sharply peaked around its maximum

If $\{N_1^*, N_2^*, \dots\}$ is configuration with largest $Q = Q^*$
then significantly different configs have much smaller Q's

I won't prove this, but to get idea:
flip a coin N times
get $\frac{N}{2}$ heads, $\pm\sqrt{N}$ or so

For $N \to \infty$, fraction of heads $\to \frac{1}{2} \pm \frac{1}{\sqrt{N}}$
Becomes very likely to get $\approx 50\%$ heads
= most likely configuration

Same holds true in general

So want to find Q^* and N^*'s.

Just take derivatives, but two complications:

1) Number of particles is fixed

Need $\sum_n N_n = N$

2) Total energy is fixed

Need $\sum_n N_n E_n = E$

Want to maximize Q subject to these constraints

Constrained optimization: use Lagrange multiplier:

Find maximum of $F(x)$, subject to $f(x) = c$

by maximizing $G(x,\lambda) = F(x) + \lambda[f(x) - c]$

with respect to x and λ

Look up in your calc book.

Still, maximizing Q directly is hard

easier to work with $\ln Q$, so that $\prod$'s $\to$ $\sum$'s

So define

$$G(N_1, N_2, \ldots) = \ln Q + \alpha\left[N - \sum_n N_n\right] + \beta\left[E - \sum_n N_n E_n\right]$$

α and β are Lagrange multipliers

Now take derivatives $\frac{\partial}{\partial N_n}$

Distinguishable particles:

$$G = \ln N! + \sum_n \left[N_n \ln d_n - \ln N_n! \right] + \alpha\left[N - \sum_n N_n\right] + \beta\left[E - \sum_n N_n E_n\right]$$

Convenient to use Stirling's approx

$$\ln N_n \approx N_n \ln N_n - N_n$$

$$G = \sum_n \left[N_n \ln d_n - N_n \ln N_n + N_n - \alpha N_n - \beta N_n E_n \right] + \ln N! + \alpha N + \beta E$$

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

Note:

$\frac{\partial}{\partial z}(z \ln z - z)$

$= \ln z + \frac{z}{z} - 1$

$= \ln z$

Set $= 0$ and solve

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

Still need to get α + β from constraints

$$\sum N_n^* = N \qquad \sum N_n^* E_n = E$$

Need to specify d_n's + E_n's to finish.

Fermions:

$$G = \sum_n \left[\ln d_n! - \ln N_n! - \ln (d_n - N_n)! \right]$$

$$+ \alpha \left[N - \sum_n N_n \right] + \beta \left[E - \sum_n N_n E_n \right]$$

Assume d_n also very large, necessary if N_n is large.

Further, assume $d_n \gg N_n$

Why?

- Can't have $d_n < N_n$ at all

- If $d_n = N_n$, Stirling works anyway, since $\ln 0! = 0$

- If $d_n > N_n$, then almost always $d_n - N_n \gg 1$ just because d_n & N_n are so huge

Then set

$$G = \sum_n \left[-N_n \ln N_n + N_n - (d_n - N_n) \ln (d_n - N_n) + d_n - N_n \right.$$

$$\left. - \alpha N_n - \beta E_n N_n \right]$$

+ constants

$$\frac{\partial G}{\partial N_n} = -\ln N_n + \ln (d_n - N_n) - \alpha - \beta E_n = 0$$

$$\ln \left(\frac{d_n}{N_n} - 1 \right) = \alpha + \beta E_n$$

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

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

$$\boxed{N_n^* = \frac{d_n}{e^{(\alpha+\beta E_n)} + 1}}$$

different from distinguishable case

I'll let you do boson case

Get $\boxed{N_n^* = \frac{d_n}{e^{(\alpha+\beta E_n)} - 1}}$

Quit writing stars now, assume $N_n = N_n^*$

To go further, consider a specific system:
particles in a box
Just like electron gas problem from last week

Label single-particle states by $\vec{k} = \left(\frac{\pi n_x}{\ell_x}, \frac{\pi n_y}{\ell_y}, \frac{\pi n_z}{\ell_z}\right)$

integers n_x, n_y, n_z

Then $E_k = \frac{\hbar^2 k^2}{2m}$

Need to solve $\sum_{\vec{k}} N_{\vec{k}} = N$

$\sum_{\vec{k}} N_{\vec{k}} E_{\vec{k}} = E$

for α & β

Convert sums to integrals
using density of states $\frac{\pi^3}{V}$ = $\frac{\#\text{ of states}}{\text{volume in } k \text{ space}}$

If we say N_k = # of particles between k and $k+dk$

then degeneracy d_k becomes # of states between k & $k+dk$

From before, $d_k = \frac{1}{8} \frac{4\pi k^2 dk}{(\pi^3/V)} = \frac{V}{2\pi^2} k^2 dk$

For distinguishable particles, need

$$N = \sum_k d_k e^{-(\alpha+\beta E_k)}$$

$$\rightarrow \int_0^\infty e^{-(\alpha+\beta E_k)} \frac{V}{2\pi^2} k^2 dk$$

$$= \frac{V}{2\pi^2} e^{-\alpha} \int_0^\infty e^{-\frac{\beta\hbar^2 k^2}{2m}} k^2 dk$$

$$u = \sqrt{\frac{\beta\hbar^2}{2m}}\, k$$

$$= \frac{V}{2\pi^2} e^{-\alpha} \left(\frac{2m}{\beta\hbar^2}\right)^{3/2} \underbrace{\int_0^\infty e^{-u^2} u^2 du}_{\text{look up } = \frac{\sqrt{\pi}}{4}}$$

then $\boxed{e^{-\alpha} = \frac{N}{V}\left(\frac{2\pi\hbar^2\beta}{m}\right)^{3/2}}$

Also need

$$E = \frac{V}{2\pi^2} e^{-\alpha} \int_0^\infty e^{-\beta \frac{\hbar^2 k^2}{2m}} \left(\frac{\hbar^2 k^2}{2m} \right) k^2 dk$$

Solve, set

$$E = \frac{3V}{2\beta} e^{-\alpha} \left(\frac{m}{2\pi \beta \hbar^2} \right)^{3/2}$$

or with $e^{-\alpha}$, $\boxed{E = \frac{3N}{2\beta}}$

Remember from thermodynamics, in an ideal gas

$$E = \frac{3}{2} N k_B T$$

Evidently, $\boxed{\beta = \frac{1}{k_B T}}$ ... system has a temperature!