Lecture 21

Quantum distribution functions

\[ \text{Bosons} \quad n_\varepsilon = \frac{1}{e^{\beta(\varepsilon - \mu)} - 1} \quad \varepsilon = \text{energy of single-particle state} \]

\[ \text{Fermions} \quad n_\varepsilon = \frac{1}{e^{\beta(\varepsilon - \mu)} + 1} \]

Give correct behavior of systems when \( n_\varepsilon \) not \( \ll 1 \)

If \( n_\varepsilon \ll 1 \), both \( \to e^{-\beta(\varepsilon - \mu)} \) classical distribution

Last time gave a sketchy microcanonical derivation

Derivation easier & better in grand canonical ensemble

Start with \( Q_N = \sum e^{-\beta E} \)

\[ E = \sum \varepsilon n_\varepsilon \]

So \( Q_N = \sum e^{-\beta \sum \varepsilon n_\varepsilon} \)

where \( \sum \varepsilon n_\varepsilon \) must satisfy \( \sum n_\varepsilon = N \)

and \( n_\varepsilon = 0 \) or \( 1 \)

for fermions
Recall that each set $E_n z^3$ corresponds to just one state for identical particles.

Constraint on $N$ makes sum impossible to evaluate.

\[ Z = \sum_{N=0}^{N_0} z^N Q_N \quad z = e^{\beta \mu} \]

\[ = \sum_2 \sum_{N_0^3} z^N \sum \frac{e^{-\beta \frac{e}{z} n \varepsilon}}{z N_0^3} \]

\[ = \sum_2 \sum_{N_0^3} \prod \left( z e^{-\beta \varepsilon} \right)^{n \varepsilon} \quad \text{used } N = \sum n \varepsilon \quad \text{all } N \text{'s} \quad \text{all allowed } n \varepsilon \text{'s,}
\]

\[ \text{constriened by } N \]

Put together, sums equivalent to single sum over all possible allowed $E_n z^3$'s

\[ Z = \sum_{N_0^3} \prod \left( z e^{-\beta \varepsilon} \right)^{n \varepsilon} \quad \text{unconstriened} \]

For bosons, each $n \varepsilon$ runs from 0 to $\infty$

\[ Q_B = \sum_{n_0=0}^{N_0} \left( z e^{-\beta \varepsilon_0} \right)^{n_0} \sum_{n_i=0}^{\infty} \left( z e^{-\beta \varepsilon_i} \right)^{n_i} \ldots \]
Each term is a geometric sum

\[ \frac{1}{1 - z e^{-\beta \varepsilon}} \left( \frac{1}{1 - z e^{-\beta \varepsilon}} \right) \ldots \]

\[ = \prod_{\varepsilon} \frac{1}{1 - z e^{-\beta \varepsilon}} \]

For fermions, each \( n_\varepsilon = 0 \) or 1

\[ \Delta_\varepsilon = (1 + z e^{-\beta \varepsilon_0})(1 + z e^{-\beta \varepsilon_1}) \ldots \]

\[ = \prod_{\varepsilon} (1 + z e^{-\beta \varepsilon}) \]

Then we can get \( n_\varepsilon \) directly:

\[ \langle n_\varepsilon \rangle = \frac{\sum \sum \frac{e^{-\beta \varepsilon_\varepsilon'} n_\varepsilon e^{-\beta \sum n_\varepsilon \varepsilon}}{Z}}{Z} \]

\[ = \frac{1}{Z} \left( -\frac{1}{\beta} \frac{\partial}{\partial n_\varepsilon} Z \right) \]

\[ = -\frac{1}{\beta} \frac{\partial}{\partial n_\varepsilon} \ln Z \]

Have \( \ln Z = \sum_{\varepsilon} \ln (1 + z e^{-\beta \varepsilon}) \)

- for boson
- for fermion

Derivative leaves only term \( \varepsilon = \varepsilon' \) in sum
\[ \langle n_z' \rangle = \frac{-1}{\beta} \left[ \frac{1 + 2(-\beta) e^{-\beta z'}}{1 + 2 e^{-\beta z'}} \right] \]

\[ = \frac{e^{-\beta z'}}{1 + 2 e^{-\beta z'}} \]

\[ = \frac{1}{e^{\beta z'} + 1} \]

or
\[ n_{z'} = \frac{1}{e^{\beta(z - 7)} + 1} \] as we got lost time

This derivation solid.

This all from Ch 6 in text

Rest of Ch 6 deals with how to handle internal degrees of freedom of gas particles (rotations & vibrations)

Interesting & useful, but I will skip

Go on to Ch 7... Bose gases

Basic point for both Bose & Fermi gases even if particles don't interact, exchange symmetry induces correlations that act like interactions
Bosons: like attractive interaction

Fermions: repulsive

Effect only significant when $N A^3 \gtrsim 1$

\[
\text{Ideal Bose gas}
\]
\[
\mathcal{Q} = \frac{\pi}{z} \left( 1 - z e^{-\beta \varepsilon} \right)
\]
\[
\mathcal{E} = -kT \ln \mathcal{Q} = PV \text{ grand potential}
\]
\[
\mathcal{E} = -kT \sum_{\mathcal{E}} \ln \left( 1 - e^{\beta \mathcal{E}} \right)
\]

Note that if we want to relate $\mu$ to $N$, we need to solve

\[
N = \sum_{\mathcal{E}} \frac{1}{z} e^{\beta \mathcal{E}} - 1
\]

Generally stuck working in terms of $\mu$

Recall that we have $\mu \geq 0$ always (assuming $\varepsilon_{min} = 0$)

as $\mu \rightarrow 0$, $H \rightarrow \infty$ so $N \rightarrow 0$

and as $\mu \rightarrow -\infty$, easy to see $N \rightarrow 0$

Get whole range
For large systems, can convert sum to integral

Need to know density of states

Get from old result from Ch 2:

\[ Z(\varepsilon) = \# \text{ of states w/ energy } \leq \varepsilon \]

\[ = \frac{V}{\hbar^3} \frac{4\pi}{3} (2m\varepsilon)^{3/2} \quad (\text{for } N=1) \]

So # of states in range d\varepsilon is

\[ a(\varepsilon) d\varepsilon = \frac{dZ}{d\varepsilon} \ d\varepsilon \]

\[ = \frac{V}{\hbar^3} 2\pi \ (2m)^{3/2} \varepsilon^{1/2} \ d\varepsilon \]

So \[ \sum_{\varepsilon} \rightarrow \int a(\varepsilon) d\varepsilon \]

Be careful, though:

see that \[ a(0) = 0 \]

This is approximately correct... really

\[ a(0) = 1 \]

assuming a unique ground state

Normally doesn't matter... what's one state, more or less?

But we know as \( N \rightarrow 0, \ N \rightarrow \infty \)

So that one state might have a lot of population in it
So best pull it out and treat separately

\[
\frac{PV}{kT} = - \sum \ln \left(1 - ze^{-\beta x}\right)
\]

\[
\Rightarrow -\ln(1 - z) - \frac{V}{h^3} \frac{1}{2\pi (2\pi)^{3/2}} \int_0^\infty z^{3/2} \ln \left(1 - ze^{-\beta x}\right) dz
\]

and

\[
N = \frac{1}{z^{1-1}} + \frac{V}{h^3} \frac{1}{2\pi (2\pi)^{3/2}} \int_0^\infty \frac{z^{1/2} dz}{z^{1-1} - 1}
\]

\[
e^{-\beta/kT} : \text{ for } \mu < kT \Rightarrow 0 \text{ a no term vanishes}
\]

\[n_0 = \frac{z}{1 - z} \text{ and } z = \frac{n_0}{n_0 + 1}\]

Note in \(\frac{PV}{kT}\) expression,

\[-\ln(1 - z) = -\ln \frac{1}{n_0 + 1}\]

\[= \ln(n_0 + 1)\]

So even as \(n \to 0, \text{ this term } \to \ln N\)

Still negligible

So we can accurately say \((x = \beta e)\)

\[
\frac{P}{kT} = -\frac{2\pi}{h^3} \left(2\pi kT\right)^{3/2} \int_0^\infty x^{1/2} \ln \left(1 - ze^{-x}\right) dx
\]

\[
= -\frac{2}{5\pi} \frac{1}{h^3} \int_0^\infty x^{1/2} \ln \left(1 - ze^{-x}\right) dx
\]
Also have
\[
\frac{N - N_0}{V} = \frac{2\pi (2m\hbar^2)}{h^3} \int_0^\infty \frac{x^{\nu/2}\, dx}{e^x - 1}
\]
\[
= \frac{2}{\sqrt{\pi}} \frac{1}{\Lambda^3} \int_0^\infty \frac{x^{\nu/2}\, dx}{e^x - 1}
\]

Can't reduce these integrals, but define Bose-Einstein functions
\[
g_\nu(x) = \frac{1}{\Gamma(\nu)} \int_0^\infty \frac{x^{\nu-1}\, dx}{e^x - 1}
\]

If we Taylor expand integrand for small \( x \) and integrate term by term, find
\[
g_\nu(x) = x + \frac{x^2}{2\nu} + \frac{x^3}{3\nu^2} + \ldots
\]
\[
g_\nu(1) = \sum_{n=1}^{\infty} \frac{1}{n^\nu} = \zeta(\nu)
\]
Riemann zeta function
\( \zeta(\nu) \) shows up in all kinds of interesting places.

Can see \( \frac{N - N_0}{V} \sim g_{3/2}(x) \)

Since \( \Gamma(\frac{3}{2}) = \frac{1}{2} \Gamma\left(\frac{1}{2}\right) = \frac{\sqrt{\pi}}{2} \), have
\[
\frac{N - N_0}{V} = \frac{1}{\Lambda^3} g_{3/2}(x)
\]
Other expression \[ \frac{\rho}{kT} = -\frac{2}{\sqrt{\pi}} \frac{1}{\Lambda^3} \int_0^\infty x^{3/2} \ln(1-ze^{-x}) \, dx \]

can be related to \( g_n \)'s:

Integrate by parts \( u = \ln(1-ze^{-x}) \)
\[ du = x^{1/2} \]
\[ dv = ze^{-x} \]
\[ v = \frac{2}{3} x^{3/2} \]

So
\[ \frac{\rho}{kT} = -\frac{2}{\sqrt{\pi}} \frac{1}{\Lambda^3} \left[ \frac{2}{3} x^{3/2} \ln(1-ze^{-x}) \right]_0^\infty \]
\[ - \int_0^\infty \frac{2}{3} \frac{x^{3/2}}{ze^{-x-1}} \, dx \]

Boundary terms \( \to 0 \)

So
\[ \frac{\rho}{kT} = \frac{4}{3\sqrt{\pi}} \frac{1}{\Lambda^3} \int_0^\infty \frac{x^{3/2}}{ze^{-x-1}} \, dx \]

Note \( \Gamma\left(\frac{5}{2}\right) = \frac{3}{2} \Gamma\left(\frac{3}{2}\right) = \frac{3\sqrt{\pi}}{4} \)
So \[ \frac{P}{kT} = \frac{1}{\Lambda^3} g_{5/2}(z) \]

\[ g_{5/2} \]

In principle, eliminate \( z \) between these two equations, get \( \frac{P}{kT} \) as function of \( N, V \)

\( \Rightarrow \) equation of state

Can't actually do in any reasonable form, but can still say plenty of interesting things

For instance,

\[ U = -\left( \frac{\partial}{\partial \rho} \ln(\tilde{\zeta}) \right)_{\tilde{z}, V} = kT^2 \frac{\partial}{\partial T} \left( \frac{\rho V}{kT} \right)_{\tilde{z}, V} \]

\[ = kT^2 V g_{5/2}(z) \frac{d}{dT} \left( \frac{1}{\Lambda^3} \right) \]

\( \Rightarrow \sim T^{3/2} \)

\[ U = \frac{3}{2} kT \frac{V}{\Lambda^3} g_{5/2}(z) \]