Lecture 21

Quantum distribution functions

Bosons $\quad n_\varepsilon = \dfrac{1}{e^{\beta(\varepsilon-\mu)}-1}$ $\qquad$ ε = energy of single-particle state

Fermions $\quad n_\varepsilon = \dfrac{1}{e^{\beta(\varepsilon-\mu)}+1}$

Give correct behavior of systems when

n_ε 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 $\quad Q_N = \sum e^{-\beta E}$

$$E = \sum_\varepsilon n_\varepsilon \varepsilon$$

So $\quad Q_N = \displaystyle\sum_{\{n_\varepsilon\}} e^{-\beta \sum_\varepsilon n_\varepsilon \varepsilon}$

where $\{n_\varepsilon\}$ must satisfy $\sum n_\varepsilon = N$

and $n_\varepsilon = 0$ or 1 for fermions

Recall that each set $\{n_\varepsilon\}$ corresponds to just one state for identical particles

Constraint on N makes sum impossible to evaluate

$\Rightarrow$ go to grand canonical

$$\mathcal{Q} = \sum_{N=0}^{\infty} z^N Q_N \qquad z = e^{\beta\mu}$$

$$= \sum_N z^N \sum_{\{n_\varepsilon\}} e^{-\beta \sum_\varepsilon n_\varepsilon \varepsilon}$$

$$= \sum_N \sum_{\{n_\varepsilon\}} \prod_\varepsilon \left(z e^{-\beta\varepsilon}\right)^{n_\varepsilon} \qquad \text{used } N = \sum n_\varepsilon$$

all N's — all allowed n_ε's, constrained by N

Put together, sums equivalent to single sum over all possible allowed $\{n_\varepsilon\}$'s

$$\mathcal{Q} = \sum_{\{n_\varepsilon\}} \prod_\varepsilon \left(z e^{-\beta\varepsilon}\right)^{n_\varepsilon}$$

unconstrained

For bosons, each n_ε runs from 0 to ∞

$$\mathcal{Q}_B = \sum_{n_0=0}^{\infty} \left(z e^{-\beta\varepsilon_0}\right)^{n_0} \sum_{n_1=0}^{\infty} \left(z e^{-\beta\varepsilon_1}\right)^{n_1} \cdots$$

Each term is a geometric sum

$$\mathcal{Z}_B = \left(\frac{1}{1-ze^{-\beta\varepsilon_0}}\right)\left(\frac{1}{1-ze^{-\beta\varepsilon_1}}\right)\cdots$$

$$= \prod_{\varepsilon} \frac{1}{1-ze^{-\beta\varepsilon}}$$

For fermions, each $n_\varepsilon = 0$ or 1

$$\mathcal{Z}_F = \left(1+ze^{-\beta\varepsilon_0}\right)\left(1+ze^{-\beta\varepsilon_1}\right)\cdots$$

$$= \prod_{\varepsilon}\left(1+ze^{-\beta\varepsilon}\right)$$

Then we can get n_ε directly:

$$\langle n_{\varepsilon'}\rangle = \frac{\sum_N \sum_{\{n_\varepsilon\}} n_{\varepsilon'}\, e^{-\beta\sum_\varepsilon n_\varepsilon \varepsilon}\, z^N}{\mathcal{Z}}$$

$$= \frac{1}{\mathcal{Z}}\left(-\frac{1}{\beta}\frac{\partial}{\partial n_{\varepsilon'}}\mathcal{Z}\right)$$

$$= -\frac{1}{\beta}\frac{\partial}{\partial n_{\varepsilon'}}\ln\mathcal{Z}$$

Have $\ln\mathcal{Z} = \mp\sum_\varepsilon \ln\left(1\mp ze^{-\beta\varepsilon}\right)$

$-$ for boson

$+$ for fermion

Derivative leaves only term $\varepsilon=\varepsilon'$ in sum

$$\langle n_{\varepsilon'} \rangle = -\frac{1}{\beta}\left[\mp \frac{\mp z(-\beta)e^{-\beta\varepsilon'}}{1 \mp z e^{-\beta\varepsilon'}}\right]$$

$$= \frac{e^{-\beta\varepsilon'}}{1 \mp z e^{-\beta\varepsilon'}}$$

$$= \frac{1}{e^{\beta\varepsilon'} z^{-1} \mp 1}$$

or $\boxed{n_\varepsilon = \frac{1}{e^{\beta(\varepsilon-\mu)} \mp 1}}$ as we got last 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 $n\Lambda^3 \gtrsim 1$

Ideal Bose gas

$$Q = \prod_{\varepsilon} (1 - z e^{-\beta\varepsilon})$$

$$\Phi = -kT \ln Q = PV \quad \text{grand potential}$$

$$= -kT \sum_{\varepsilon} \ln(1 - e^{\beta(\mu-\varepsilon)})$$

Note that if we want to relate μ to N, need to solve

$$N = \sum n_{\varepsilon} = \sum_{\varepsilon} \frac{1}{e^{\beta(\varepsilon-\mu)} - 1}$$

generally stuck working in terms of μ

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

as $\mu \to 0$, $n_0 \to \infty$ so $N \to \infty$

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

Get whole range

For large system, can convert sum to integral

Need to know density of states

Get from old result from Ch 2:

$$\Sigma(\varepsilon) = \text{\# of states w/ energy} \le \varepsilon$$

$$= \frac{V}{h^3}\frac{4\pi}{3}(2m\varepsilon)^{3/2}$$

(for $N=1$)

So # of states in range $d\varepsilon$ is

$$a(\varepsilon)d\varepsilon = \frac{d\Sigma}{d\varepsilon}d\varepsilon$$

$$= \frac{V}{h^3}2\pi(2m)^{3/2}\varepsilon^{1/2}d\varepsilon$$

So $\sum_\varepsilon \to \int a(\varepsilon)d\varepsilon$

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 $\mu \to 0$, $n_0 \to \infty$

So that one state might have a lot of population in it

So best pull it out and treat separately

So $$\frac{PV}{kT} = -\sum_{\varepsilon} \ln(1 - ze^{-\beta\varepsilon})$$

$$\rightarrow -\ln(1-z) - \frac{V}{h^3} 2\pi (2m)^{3/2} \int_0^\infty \varepsilon^{1/2} \ln(1 - ze^{-\beta\varepsilon})\, d\varepsilon$$

and
$$N = \frac{1}{z^{-1}-1} + \frac{V}{h^3} 2\pi (2m)^{3/2} \int_0^\infty \frac{\varepsilon^{1/2} d\varepsilon}{z^{-1}e^{\beta\varepsilon} - 1}$$

$z = e^{\mu/kT}$: for $\mu \ll kT$ $z \to 0$ & n_0 term vanishes

$$n_0 = \frac{z}{1-z} \quad \text{and} \quad z = \frac{n_0}{n_0+1}$$

Note in $\frac{PV}{kT}$ expression,

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

$$= \ln(n_0+1)$$

So even as $\mu \to 0$, this term $\to \ln N$

Still negligible

So we can accurately say $(x = \beta\varepsilon)$

$$\frac{P}{kT} = -\frac{2\pi}{h^3} (2mkT)^{3/2} \int_0^\infty x^{1/2} \ln(1 - ze^{-x})\, dx$$

$$= -\frac{2}{\sqrt{\pi}} \frac{1}{\lambda^3} \int_0^\infty x^{1/2} \ln(1 - ze^{-x})\, dx$$

Also have

$$\frac{N-N_0}{V} = \frac{2\pi(2mkT)^{3/2}}{h^3} \int_0^\infty \frac{x^{1/2}\,dx}{z^{-1}e^x - 1}$$

$$= \frac{2}{\sqrt{\pi}} \frac{1}{\Lambda^3} \int_0^\infty \frac{x^{1/2}\,dx}{z^{-1}e^x - 1}$$

Can't reduce these integrals, but define Bose-Einstein functions

$$g_\nu(z) = \frac{1}{\Gamma(\nu)} \int_0^\infty \frac{x^{\nu-1}}{z^{-1}e^x - 1}\,dx$$

If we Taylor expand integrand for small z and integrate term by term, find

$$g_\nu(z) = z + \frac{z^2}{2^\nu} + \frac{z^3}{3^\nu} + \ldots$$

$$g_\nu(1) = \sum_{n=1}^\infty \frac{1}{n^\nu} = \zeta(\nu)$$

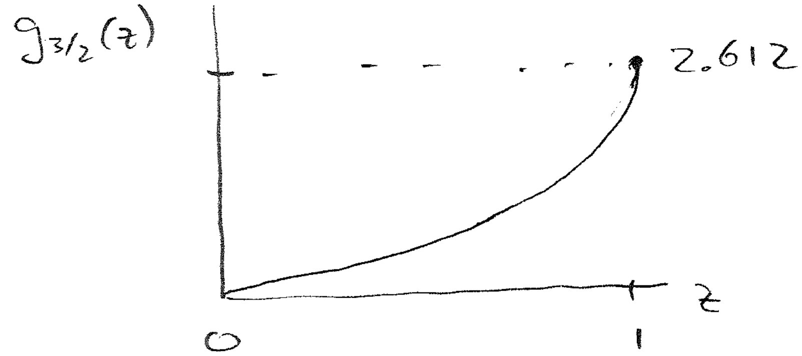
Riemann zeta function

$\zeta(\nu)$ shows up in all kind of interesting places.

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

Since $\Gamma(\frac{3}{2}) = \frac{1}{2}\Gamma(\frac{1}{2}) = \frac{\sqrt{\pi}}{2}$, have

$$\boxed{\frac{N-N_0}{V} = \frac{1}{\Lambda^3} g_{3/2}(z)}$$



Other expression $\frac{P}{kT} = -\frac{2}{\sqrt{\pi}} \frac{1}{\Lambda^3} \int_0^\infty x^{1/2} \ln(1 - z e^{-x})\, dx$

can be related to g_ν's:

Integrate by parts $u = \ln(1 - z e^{-x})$

$dv = x^{1/2}$

$$du = \frac{z e^{-x}}{1 - z e^{-x}} = \frac{1}{z^{-1} e^x - 1}$$

$$v = \frac{2}{3} x^{3/2}$$

So

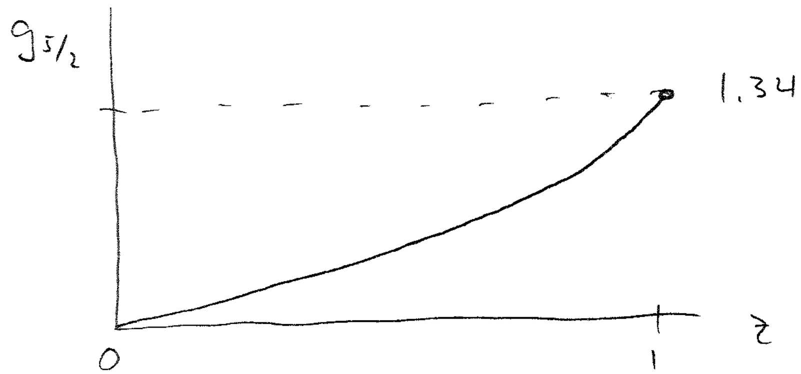
$$\frac{P}{kT} = -\frac{2}{\sqrt{\pi}} \frac{1}{\Lambda^3} \left[\frac{2}{3} x^{3/2} \ln(1 - z e^{-x}) \Big|_0^\infty - \int_0^\infty \frac{2}{3} \frac{x^{3/2}}{z^{-1} e^x - 1}\, dx \right]$$

Boundary terms $\to 0$

So $$\frac{P}{kT} = \frac{4}{3\sqrt{\pi}} \frac{1}{\Lambda^3} \int_0^\infty \frac{x^{3/2}}{z^{-1} e^x - 1}\, dx$$

Note $\Gamma(\frac{5}{2}) = \frac{3}{2} \Gamma(\frac{3}{2}) = \frac{3\sqrt{\pi}}{4}$

So $$\boxed{\frac{P}{kT} = \frac{1}{\lambda^3}\, g_{5/2}(z)}$$



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,

$$U = -\left(\frac{\partial}{\partial \beta} \ln \mathcal{Q}\right)_{z,V} = kT^2 \frac{\partial}{\partial T}\left(\frac{PV}{kT}\right)_{z,V}$$

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

$\sim T^{3/2}$

$$\boxed{U = \frac{3}{2} kT \frac{V}{\lambda^3} g_{5/2}(z)}$$