§14. Quantum Ideal Gases.

14.1 Partition function

All our calculations so far, whenever we wanted to compute explicitly the partition function for an ideal gas of indistinguishable particles, relied on the assumption that the probability of more than one particle occupying any given single-particle energy level was negligible (classical limit) — see p. 89.
We will now relax this assumption and do an honest job calculating $\mathcal{Z}$ for quantum gases.
We will use the grand-canonical ensemble as we know we can later specialise to fixed N if we wish.

$$\mathcal{Z} = \sum_{\alpha} e^{-\beta(E_\alpha - \mu N_\alpha)}$$

Suppose we know (from QM) the microstates and the corresponding energy levels of one particle:

$$i \Rightarrow \varepsilon_i$$

Then microstates, energy levels and particle numbers for the assemblage of many particles are

$$\alpha = \{n_1, n_2, \dots n_i, \dots\} \quad \text{occupation \#'s of the 1-particle states } i$$

$$E_\alpha = \sum_i n_i \varepsilon_i \quad \text{total energy}$$

$$N_\alpha = \sum_i n_i \quad \text{total \# of particles } (= N \text{ if fixed})$$

Then $\mathcal{Z} = \sum_{\{n_i\}} e^{-\beta \sum_i n_i(\varepsilon_i - \mu)} =$

$$= \sum_{\{n_i\}} \prod_i e^{-\beta n_i(\varepsilon_i-\mu)} = \underbrace{\prod_i \sum_{n_i=0,1,\ldots}}_{} \left[e^{-\beta(\varepsilon_i-\mu)}\right]^{n_i}$$

product of sums = sum of products

all possible values for occ. numbers n_i

QM teaches us that there are two types of particle possible: e.g. photons (spin 1), ^4He atoms (spin 0)...

bosons integer spin n_i = any integer number

fermions half-int. spin $n_i = 0, 1$ Pauli exclusion principle

$e, n, p, {}^3He$ etc. (spin $\frac{1}{2}$)...

(no more than 1 particle in any given state)

[The latter is an example of quantum correlation: while particles are non-interacting, the system as a whole "knows" which energy levels are occupied and so any new particles cannot occupy them.]

We get then

$$\mathcal{Z} = \begin{cases} \prod_i \left[1 + e^{-\beta(\varepsilon_i-\mu)}\right] & \text{fermions } n_i = 0, 1 \\ \prod_i \dfrac{1}{1 - e^{-\beta(\varepsilon_i-\mu)}} & \text{bosons } n_i = 0,1,2,3\ldots\infty \\ & \text{(geom. progression)} \end{cases}$$

or $\boxed{\ln \mathcal{Z} = \pm \sum_i \ln\left[1 \pm e^{-\beta(\varepsilon_i-\mu)}\right]}$ + fermions, − bosons

Simple explanation of ~~[illegible]~~ bosons and fermions:

- consider a 2-particle wave function

$$\psi(1,2)$$

1st particle in state 1

2nd particle in state 2

- swap the particles: $\psi(1,2) \to \psi(2,1)$
- since particles are indistinguishable, probability density cannot change under this operation:

$$|\psi(1,2)|^2 = |\psi(2,1)|^2$$

hence $\psi(2,1) = e^{i\phi}\,\psi(1,2) \overset{\text{swap again}}{=} e^{i2\phi}\,\psi(2,1)$

so $e^{i2\phi} = 1 \Rightarrow e^{i\phi} = \pm 1$ (technically speaking this only works in 3D)

↳ see Blundell §29.1

$$\boxed{\psi(2,1) = \pm\,\psi(1,2)}$$

(+) bosons

(−) fermions – Pauli excl. principle basically follows from the fact that if states 1, 2 are the same, $\psi(1,1) = -\psi(1,1) \Rightarrow \psi(1,1) = 0$

So two particles cannot be in the same state

[see LL §61 of Vol. 3 QM for rigorous generalization to N particles etc.]

14.2 Occupation # Statistics → Thermodynamics

The most useful consequence of this formula turns out to be our ability to calculate mean occupation numbers (in terms of which we can then calculate ~~everything~~ all thermodynamical quantities)

$$\bar{n}_i = \langle n_i \rangle = \frac{1}{\mathcal{Z}} \sum_{\{n_j\}} n_i \, e^{-\beta \sum_j n_j (\varepsilon_j - \mu)} = -\frac{1}{\beta} \frac{\partial \ln \mathcal{Z}}{\partial \varepsilon_i}$$

$$\boxed{\bar{n}_i = \frac{1}{e^{\beta(\varepsilon_i - \mu)} \pm 1}}$$

⊕ Fermi-Dirac statistics

⊖ Bose-Einstein statistics

~~[illegible]~~ We can now calculate everything we ever wanted to know:

- chemical potential: ~~[illegible]~~

$$\boxed{\bar{N} = \sum_i \bar{n}_i} \quad \text{equ for } \mu \qquad \text{(Ex.)} \qquad \Rightarrow \text{eq (1) p. 126}$$

$$\left[\text{indeed, from p. 105, } \bar{N} = \frac{1}{\beta}\left(\frac{\partial \ln \mathcal{Z}}{\partial \mu}\right)_\beta \right]$$

hence heat capacities

- energy:

$$\boxed{U = \sum_i \varepsilon_i \bar{n}_i} \qquad \text{(Ex.)} \qquad \Rightarrow \text{eq. (2) p. 126}$$

$$\left[\text{indeed, from p. 105, } U = -\left(\frac{\partial \ln \mathcal{Z}}{\partial \beta}\right)_\mu + \mu \bar{N} \right]$$

- entropy: from p. 106,

Ex. prove this!

$$S = -\frac{1}{T}\left(\underset{\substack{\uparrow \\ -k_BT\ln\mathcal{Z}}}{\Phi} - U + \mu \bar{N}\right) = -k_B \sum_i \left[\bar{n}_i \ln \bar{n}_i \pm (1 \mp \bar{n}_i) \ln (1 \mp \bar{n}_i)\right]$$

grand potential $= \pm k_B T \sum_i \ln (1 \mp \bar{n}_i)$

HW

Proof. $\Phi = \mp k_B T \sum_i \ln\left[1 \pm e^{-\beta(\varepsilon_i-\mu)}\right] =$

$$= \mp k_B T \sum_i \ln e^{-\beta(\varepsilon_i-\mu)} \underbrace{\left[e^{\beta(\varepsilon_i-\mu)} \pm 1\right]}_{= \frac{1}{\bar{n}_i}} =$$

$$= \mp k_B T \sum_i \Big[\underbrace{-\beta(\varepsilon_i-\mu)}_{= \ln\left(\frac{1}{\bar{n}_i} \mp 1\right) = \ln(1\mp\bar{n}_i) - \cancel{\ln \bar{n}_i}} - \cancel{\ln \bar{n}_i}\Big] = \pm k_B T \sum_i \ln(1\mp\bar{n}_i)$$

$$U - \mu\bar{N} = \sum_i (\varepsilon_i-\mu)\bar{n}_i = \frac{1}{\beta}\sum_i \left[\ln(1\mp\bar{n}_i) - \ln\bar{n}_i\right]\bar{n}_i$$

So

$$S = -\frac{1}{T}\left(\Phi - U + \mu\bar{N}\right) =$$

$$= \mp k_B \sum_i \ln(1\mp\bar{n}_i) + k_B \sum_i \left[\ln(1\mp\bar{n}_i) - \ln\bar{n}_i\right]\bar{n}_i$$

$$= k_B \sum_i \left[-\bar{n}_i \ln\bar{n}_i \mp (1\mp\bar{n}_i)\ln(1\mp\bar{n}_i)\right]$$

$$= -k_B \sum_i \left[\bar{n}_i \ln\bar{n}_i \pm (1\mp\bar{n}_i)\ln(1\mp\bar{n}_i)\right]$$

q.e.d.

- Equation of state: since $\Phi = -PV$,

$$\boxed{P = \mp \frac{k_B T}{V} \sum_i \ln(1\mp\bar{n}_i)}$$

$\Rightarrow$ eq. (4) p. 127

(classical limit: $\bar{n}_i \ll 1 \Rightarrow P \approx \mp \frac{k_B T}{V}\sum_i (\mp\bar{n}_i) = \frac{k_B T}{V}\bar{N}$ ok!)

14.3 Preview of various limits

Let us anticipate quickly what we are going to discover about the behaviour of quantum gases at high and low temperatures.

The temperature dependence of $\bar{n}_i$ comes from β and from μ, which is determined via $\bar{N} = \sum_i \bar{n}_i$.

High temperatures. $T \to \infty$. what does this mean? In this limit, we expect quantum correlations to be negligible.

On p. 89, we had a condition for this:

$$\underbrace{n}_{= e^{\beta\mu}} \lambda_{th}^3 \ll 1, \quad \lambda_{th} = \hbar \sqrt{\frac{2\pi}{m k_B T}}$$

(see p. 110c)

so high temperature and low density

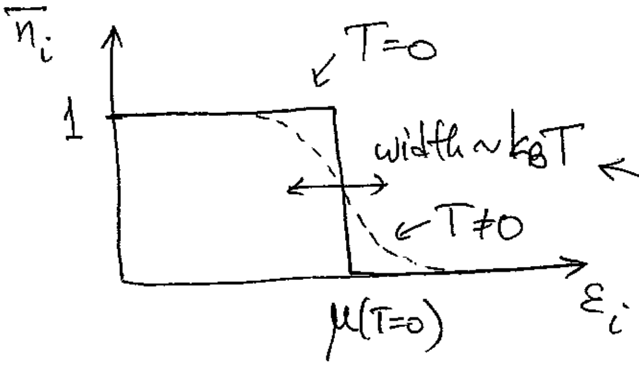
Then
$$\bar{n}_i = \frac{1}{\underbrace{e^{-\beta\mu}}_{\text{large}} e^{\beta \varepsilon_i} \pm 1} \approx e^{\beta\mu} e^{-\beta\varepsilon_i}$$

For $\varepsilon_i = \frac{mv^2}{2}$, this gives $\bar{n}_i \propto e^{-\frac{mv^2}{2k_B T}}$

– we recover Maxwell's distribution (I will sort out the prefactor later). This is natural: the velocity distribution function was indeed just the (fractional) number of particles with a given velocity (i.e. in a given state).

Fermions at low temperature. $\beta \to \infty$, $T=0$.

$$\overline{n}_i = \frac{1}{e^{\beta(\varepsilon_i - \mu)}+1} \longrightarrow \begin{cases} 1 & \text{if } \varepsilon_i < \mu(0) \\ 0 & \text{if } \varepsilon_i > \mu(0) \end{cases}$$



so they stack up to

$\varepsilon_i = \mu(T=0) \equiv \varepsilon_F$

Fermi energy

"low T" means $k_BT \ll \varepsilon_F$

Because the distribution at T=0 is so simple, it will be easy to calculate things.

Bosons at low temperature.

$$\overline{n}_i = \frac{1}{e^{\beta(\varepsilon_i-\mu)}-1}$$

First of all, note that we must have $e^{\beta(\varepsilon_i-\mu)} > 1$ for all energy levels, otherwise $\overline{n}_i$ will turn ∞ or negative. Therefore $\mu < \varepsilon_0$ - lowest energy level.

Intuitively, we expect, as $T \to 0$,

$\overline{n}_0 \to \overline{N}$ and $\overline{n}_i \to 0$ for all higher energy levels, i.e. the particles will condense in the lowest energy state. But to sort out exactly how this and all the other things previewed above happen, we need to learn how to calculate $\mu(T)$, i.e., to solve the equation

$$\sum_i \overline{n}_i = \overline{N}.$$

<u>Note</u>. We can do all this at fixed N basically by just replacing $\bar{N} \to N$.

It is possible in principle to derive the same formulae directly from canonical, rather than grand-canonical formulation, but it is much harder mathematically because on p 121, the sum $\sum_{\{n_i\}}$ must be done holding $\sum_i n_i = N$ exactly fixed. The method is due to Darwin & Fowler and explained in Schrödinger's book and in J. Binney's notes.

~~[illegible]~~

<u>Photons</u>. They are bosons, with $\varepsilon = pc$ and $m=0$. Furthermore their # is not fixed at all, the system can create or destroy them and will do to achieve equilibrium. At fixed T and V, this means that $F \to$ min and so

[no energy or entropy cost of changing the # of particles]

$$\mu = \left(\frac{\partial F}{\partial \bar{N}}\right)_{V,T} = 0 \quad (\text{see p. 109})$$

$dF = -SdT - pdV + \mu d\bar{N}$

Thus, everything we learn about bosons (at finite T) will apply to a box of photons if we set $\mu=0$ and consider the ultrarelativistic limit (see AB's lectures on b.b. radiation).

Lecture 4 ended here.

14.4 Calculations in the Continuous Limit

Ok, so we need to compute sums like $\overline{N} = \sum_i \overline{n}_i$, where i indexes single particle states.

we'll drop the overbar from now on.

These are set by the particle's momentum:

$\vec{p} = \hbar \vec{k}$ (we'll consider gas in a box, so $\vec{k}$'s are discrete, see pp. 84-85)

and ~~angular momentum~~ spin S (or/and angular momentum), whose projection on an axis can take values $-S, \dots, S$, where S is ~~integer~~ integer or half-integer — $(2S+1)$ states in total.

2 for $S=\frac{1}{2}$

$\overline{n}_i$ depends only on energy: $\varepsilon^{(k)} = \frac{\vec{p}^2}{2m} = \frac{\hbar^2 \vec{k}^2}{2m}$ for a non-relativistic particle

[for ~~...~~ ultrarelativistic, $\varepsilon^{(k)} = \hbar k c$; e.g. photons

in general, $\varepsilon^{(k)} = \sqrt{m^2c^4 + \hbar^2 k^2 c^2}$]

Therefore,

$$N = \sum_i \overline{n}_i = (2S+1) \sum_{\vec{k}} \overbrace{\frac{1}{e^{\beta[\varepsilon(k)-\mu]} \pm 1}}^{= n_{\vec{k}}} =$$

$$\sum_{\vec{k}} = \frac{V}{(2\pi)^3} \int d^3\vec{k} = \frac{V}{2\pi^2} \int_0^\infty dk\, k^2$$

$g(k)$ density of states $\equiv$

$$= \frac{(2S+1)V}{2\pi^2} \int_0^\infty \frac{dk\, k^2}{e^{\beta[\varepsilon(k)-\mu]} \pm 1} = \int_0^\infty dk\, g(k)\, n_{\vec{k}} .$$

Considering the non-relativistic case, note that

$$d\varepsilon = \frac{\hbar^2 k\, dk}{m} \quad \text{and} \quad k = \frac{\sqrt{2m}}{\hbar} \sqrt{\varepsilon}, \text{ so}$$

$$g(k)\, dk = \frac{(2S+1)V}{2\pi^2} \frac{m}{\hbar^2} d\varepsilon \cdot \frac{\sqrt{2m}}{\hbar} \sqrt{\varepsilon} = \underbrace{\frac{(2S+1)V m^{3/2}}{\pi^2 \sqrt{2}\, \hbar^3} \sqrt{\varepsilon}}_{\equiv g(\varepsilon)}\, d\varepsilon$$

This gives

$$N = \frac{(2S+1)Vm^{3/2}}{\pi^2\sqrt{2}\,\hbar^3}\int_0^\infty \frac{d\varepsilon\sqrt{\varepsilon}}{e^{\beta(\varepsilon-\mu)}\pm 1} \overset{\text{let } x=\beta\varepsilon}{=}$$

$$= \underbrace{\frac{(2S+1)V}{(2\pi)^2}\left(\frac{2mk_BT}{\hbar^2}\right)^{3/2}}_{=\ \frac{2(2S+1)}{\sqrt{\pi}}\frac{V}{\lambda_{th}^3}} \underbrace{\left\{\int_0^\infty \frac{dx\sqrt{x}}{e^x \underbrace{e^{-\beta\mu}}_{=\ \frac{1}{z}}\pm 1}\right\}}_{\text{this integral is a function only of } z} \ \text{Some function } f(\beta\mu)$$

$z = e^{\beta\mu}$ fugacity

So, this equation:

$$\boxed{N = \frac{2(2S+1)}{\sqrt{\pi}}\frac{V}{\lambda_{th}^3}\int_0^\infty \frac{dx\sqrt{x}}{e^{x-\beta\mu}\pm 1}} \qquad (1)$$

implicitly determines the ch. potential μ.

It is also useful to calculate energy:

$$U = \sum_i \varepsilon_i \bar{n}_i \underset{\substack{\text{exactly}\\ \text{analogous}\\ \text{calculation}}}{=} \frac{(2S+1)Vm^{3/2}}{\pi^2\sqrt{2}\,\hbar^3}\int_0^\infty \frac{d\varepsilon\,\varepsilon^{3/2}}{e^{\beta(\varepsilon-\mu)}\pm 1} =$$

$$= \frac{2(2S+1)}{\sqrt{\pi}}\frac{V}{\lambda_{th}^3}k_BT\int_0^\infty \frac{dx\,x^{3/2}}{e^{x-\beta\mu}\pm 1} \qquad (2)$$

and the grand potential:

$$\Phi = -k_BT\ln\mathcal{Z} = \mp k_BT\sum_i \ln\left[1\pm e^{-\beta(\varepsilon_i-\mu)}\right] =$$

$$= \mp k_B T \frac{(2S+1)Vm^{3/2}}{\pi^2\sqrt{2}\hbar^3}\int_0^\infty d\varepsilon\sqrt{\varepsilon}\ln\left[1\pm e^{-\beta(\varepsilon-\mu)}\right]$$

by parts

$$= \mp k_B T \frac{(2S+1)Vm^{3/2}}{\pi^2\sqrt{2}\hbar^3}\frac{2}{3}\int_0^\infty d\varepsilon\,\varepsilon^{3/2}\frac{\pm e^{-\beta(\varepsilon-\mu)}(-\beta)}{1\pm e^{-\beta(\varepsilon-\mu)}}$$

$$= -\frac{2}{3}\frac{(2S+1)Vm^{3/2}}{\pi^2\sqrt{2}\hbar^3}\int_0^\infty \frac{d\varepsilon\,\varepsilon^{3/2}}{e^{\beta(\varepsilon-\mu)}\pm 1} \qquad (3)$$

From this, we can derive several important <u>consequences</u>:

1) $\Phi = -\frac{2}{3}U$ (see formula (2) on p. 126)

$\Phi = -PV$ (p. 110), so $\boxed{U = \frac{3}{2}PV}$ or $P = \frac{2}{3}\frac{U}{V}$ ($\frac{U}{V}$: energy density)

<u>completely generally</u> (indeed, for classical gas we know $p = nk_BT$ and $U = \frac{3}{2}Nk_BT$, as it should be)

2) <u>Equation of state</u>:

$p = -\frac{\Phi}{V}$, so, from (3),

$$\boxed{p = \frac{2}{3}\frac{(2S+1)m^{3/2}}{\pi^2\sqrt{2}\hbar^3}\int_0^\infty\frac{d\varepsilon\,\varepsilon^{3/2}}{e^{\beta(\varepsilon-\mu)}\pm 1}} \qquad (4)$$

– this is the equation of state, if considered with (1) for μ.

3) <u>Adiabatic process</u>:

We can prove that $\boxed{PV^{5/3} = \text{const}}$

when $S = \text{const}$, <u>completely generally</u>.

(and $N = \text{const}$)

Proof. Since $d\Phi = -SdT - pdV - Nd\mu$ (p.107),

$$S = -\left(\frac{\partial \Phi}{\partial T}\right)_{V,\mu}$$

From (3),

$$\Phi = -\frac{2}{3}\,\frac{(2S+1)Vm^{3/2}(k_BT)^{5/2}}{\pi^2\sqrt{2}\,\hbar^3}\int_0^\infty \frac{dx\,x^{3/2}}{e^{x-\beta\mu}\pm 1} =$$

$$= VT^{5/2} f\left(\frac{\mu}{T}\right)$$

function only of one argument

Then

$$S = -V\left[\frac{5}{2}T^{3/2} f\left(\frac{\mu}{T}\right) - f'\left(\frac{\mu}{T}\right)\frac{\mu}{T^2}\cdot T^{5/2}\right] =$$

$$= -VT^{3/2}\left[\frac{5}{2} f\left(\frac{\mu}{T}\right) - \frac{\mu}{T} f'\left(\frac{\mu}{T}\right)\right]$$

We also know that

$$N = -\left(\frac{\partial \Phi}{\partial \mu}\right)_{T,V} = -VT^{5/2} f'\left(\frac{\mu}{T}\right)\frac{1}{T} =$$

$$= -VT^{3/2} f'\left(\frac{\mu}{T}\right)$$

So $\dfrac{S}{N} = \dfrac{5}{2}\dfrac{f(\mu/T)}{f'(\mu/T)} - \dfrac{\mu}{T}$ – function only of $\dfrac{\mu}{T}$

Adiabatic process with fixed # of particles:

$$S, N = \text{const} \Rightarrow \frac{\mu}{T} = \text{const}$$

Therefore $VT^{3/2} = \text{const}$.

Finally, $\Phi = -PV \Rightarrow P = -T^{5/2} f\left(\frac{\mu}{T}\right)$

and so $PT^{-5/2} = \text{const}$.

Combining these results, we get $PV^{5/3} = \text{const}$ q.e.d.

Note. $\frac{5}{3}$ survives, but, unlike for ideal gas, it is not (in general) equal to C_p/C_V! [which has to be calculated from (2) and ~~[illegible]~~ equation of state.]

14.5. Classical Limit

Let us now do as promised on p.123 and recover Maxwell's distribution in the classical limit. Consider (1):

$$\underbrace{\int_0^\infty \frac{dx\sqrt{x}}{e^{x-\beta\mu}\pm 1}}_{\text{unknown } f(\beta\mu)} = \frac{N}{V}\frac{\sqrt{\pi}}{2(2s+1)}\lambda_{th}^3 = n\frac{\sqrt{\pi}}{2(2s+1)}\hbar^3\left(\frac{2\pi}{mk_BT}\right)^{3/2}$$

unknown $f(\beta\mu) \to 0$ if $n \to 0$ and $T \to \infty$

Thus, in the dilute hot gas, we must have $f(\beta\mu) \to 0$, which is achievable by $e^{-\beta\mu} \gg 1$.

This gives us $f(\beta\mu) \approx e^{\beta\mu} \underbrace{\int_0^\infty dx\sqrt{x}\,e^{-x}}_{=\sqrt{\pi}/2 \text{ (exercise!)}}$

and so

$$e^{\beta\mu} \approx \frac{n\lambda_{th}^3}{2s+1}$$

$$\boxed{\mu \approx k_BT \ln \frac{n\lambda_{th}^3}{2s+1}}$$

Same formula as on p 110c except for the $2s+1$, which we did not include before, but could have done easily.

Note. Applying $e^{\beta\mu} \ll 1$ to $\mathcal{Z}$, we get, from p. 121:

$$\ln \mathcal{Z} \approx \sum_i e^{\beta\mu} e^{-\beta\varepsilon_i} = e^{\beta\mu} Z_1$$

$$\mathcal{Z} \approx e^{Z_1 e^{\beta\mu}}$$ exactly the formula on p. 110b

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For a situation with fixed N, we get (see p. 106)

$$Z_N = \frac{\mathcal{Z}}{(e^{\beta\mu})^N} = \frac{e^{Z_1 e^{\beta\mu}}}{(e^{\beta\mu})^N} = \frac{e^N}{(N/Z_1)^N} = \frac{Z_1^N}{N^N e^{-N}}$$

$\simeq N!$ as it should be.

and $Z_1 = (2s+1)\dfrac{V}{\lambda_{th}^3}$, $\quad e^{\beta\mu} = \dfrac{n\lambda_{th}^3}{2s+1} = \dfrac{N}{Z_1}$

OK, so everything is consistent.

- The same approximation procedure (as on p. 129) applied to (4) gives $\underset{\uparrow}{p = nk_BT}$ (exercise).

  ideal gas equ of state

- Occupation number:

$$\bar{n}_i = \frac{1}{e^{\beta(\varepsilon_i-\mu)}\pm 1} \approx e^{-\beta\varepsilon_i}\underbrace{e^{\beta\mu}}_{=\frac{n\lambda_{th}^3}{2s+1}}$$

Now $\bar{n}_i$ is # of particles per state i, which means (det'd by $\vec{k}$ and s) that the number of particles per unit volume per wave vector is

$$\frac{1}{V}\cdot(2s+1)\frac{V}{(2\pi)^3}\,d^3\vec{k}\cdot \overbrace{e^{-\beta\varepsilon(k)}e^{\beta\mu}}^{=\bar{n}_i} =$$

$$= \frac{n\lambda_{th}^3}{(2\pi)^3}\,e^{-\beta\cdot\frac{mv^2}{2}}\,d^3\!\left(\frac{m\vec{v}}{\hbar}\right) = \frac{n}{(2\pi)^3}\cancel{\hbar^3}\left(\frac{2\pi}{mk_BT}\right)^{3/2}\frac{m^3}{\cancel{\hbar^3}}\,e^{-\frac{mv^2}{2k_BT}}\,d^3\vec{v}$$

$$= \frac{n}{(2\pi k_BT/m)^{3/2}}\,e^{-\frac{mv^2}{2k_BT}}\,d^3\vec{v} = \underbrace{\frac{n}{(\pi v_{th}^2)^{3/2}}\,e^{-\frac{v^2}{v_{th}^2}}}_{=F(\vec{v})}\,d^3\vec{v}$$

Note how nicely all the quantum things ($\hbar$'s and spins) have cancelled out.

$F(\vec{v})$ Maxwellian, q.e.d.

The classical limit is valid when $\boxed{n\lambda_{th}^3 \ll 1}$ (cf. p. 89)

i.e. $e^{\beta\mu} \ll 1$ (p. 129)

Entropy

Note that in the classical limit $\overline{n}_i \ll 1$
(so, as argued before, probability of more than one – or even one! – particle in any given energy state is very small).

Therefore, from p. 122, entropy

$$S \approx -k_B \sum_i \overline{n}_i \ln \overline{n}_i$$

→ should be able to get Sackur–Tetrode formula from this by substituting $\overline{n}_i \approx e^{-\beta\varepsilon_i} \dfrac{n\lambda_{th}^3}{2s+1}$

(exercise)

$$\lambda_{th} = \hbar\sqrt{\frac{2\pi}{mk_BT}}$$

14.6 Degeneration

So, the condition for the classical limit to break down is $n\lambda_{th}^3 \sim 1$ (i.e. high enough density and low enough temperature).
As I explained before (p.89), this means that

$$\underset{\text{per particle}}{\#\text{ of quantum states}} \sim \frac{V}{\lambda_{th}^3} \sim N \;\#\text{ of particles}$$

so we can no longer argue that two particles are extremely unlikely to compete for the same state (i.e. $\bar{n}_i$'s are no longer small).
Here is another, perhaps more illuminating, interpretation (which I in fact already mentioned on p.16a).
The particle's average energy is

$$\left\langle \frac{p^2}{2m} \right\rangle \sim \frac{3}{2} k_BT$$

So the mean square momentum is

$$\langle p^2 \rangle \sim 3k_BTm$$

Clearly the quantum uncertainty in the determination of its momentum must be less $\langle p^2\rangle^{1/2}$ (otherwise the spread in momenta would be larger and so $\langle p^2\rangle$ would be larger), so

$$\Delta p \lesssim (mk_BT)^{1/2} \quad \text{(ignoring numerical coefficients)}$$

But the uncertainty principle tells us Δp is related to the position uncertainty Δx as

$$\Delta p \Delta x \sim \hbar$$

and so
$$\Delta x \gtrsim \frac{\hbar}{\sqrt{m k_B T}} \sim \lambda_{th}$$

Now the average distance between particles is $\ell \sim (V/N)^{1/3} = n^{-1/3}$ and so

$\boxed{\frac{\Delta x}{\ell} \sim \lambda_{th} n^{1/3}}$ — in the classical limit, this is small ($n\lambda_{th}^3 \ll 1$), so we can talk about granulated structure of our gas. When $n\lambda_{th}^3 \sim 1$, the particles become completely blurred. The gas under these conditions enters a quantum "degenerate" state.

Lecture 5 ended here.

So, what do we do when $n\lambda_{th}^3$ is not small? We must learn how to calculate the two integrals (1) and (2) [or (3)]. Then we will be able, for example, to calculate the equation of state or the heat capacity of our gas.

Weak degeneration. We can expand in $e^{\beta\mu}$ small but finite and get corrections to the standard ideal gas formulae. This is not terribly interesting (but is a good exercise).

Strong degeneration. What if $e^{\beta\mu} \gg 1$? We'll see this is only possible for fermions, while bosons will have to be analysed separately.

Before we deal with the strongly degenerate case, let's estimate whether it is actually a relevant limit for something. Using (in the classical limit) $p = nk_BT$,

$$n\lambda_{th}^3 = \frac{p}{k_BT}\hbar^3\left(\frac{2\pi}{mk_BT}\right)^{3/2} = \frac{p}{m^{3/2}T^{5/2}}\frac{\hbar^3(2\pi)^{3/2}}{k_B^{5/2}}$$

$$\approx\left(\frac{p}{1\,\mathrm{atm}}\right)\left(\frac{T}{300\,\mathrm{K}}\right)^{-5/2}\left(\frac{m}{m_p}\right)^{-3/2}\cdot 2.5\cdot 10^{-5}$$

So, for example,

air at room T and p : $n\lambda_{th}^3 \sim 10^{-6} \ll 1$ safely classical

still at room p {

^{4}He at 4K : $n\lambda_{th}^3 \sim 0.15$ getting dangerously close to degeneration

electrons in metals : $n\lambda_{th}^3 \sim 2$, which suggests they are not classical at all – in fact, we should not then have used $p = nk_BT$! – but we know their density : roughly, $n \sim 10^{28}\,\mathrm{m}^{-3}$. Then

$n\lambda_{th}^3 \sim 10^4 \gg 1$ so they are completely degenerate! [high density, small mass]

(at $T = 300\,\mathrm{K}$)

We can calculate the temperature at which they would be classical :

$$n\lambda_{th}^3 \sim 1 \Rightarrow T \sim \frac{2\pi n^{2/3}\hbar^2}{m_e k_B} \sim 10^4\,\mathrm{K}$$

So this is one clear application of degenerate Fermi gas. Another is electrons in white dwarfs and neutrons in neutron stars [Chandrasekhar's theory of the stability of stars]