3. The Thermal Physics of the Ideal Classical Gas

(Mandl 7.1-7.6, B&S 5.9, 6.5, 7.4, K&K p72-77)
To show amongst other things that
$pV = nk_BT$
in the classical limit.

3.1 What is the classical limit?

Typical energy of particles in a classical gas $\sim k_BT = \left\langle \frac{p^2}{2m} \right\rangle$

$p \sim \left(2Mk_bT\right)^{1/2}$
de Broglie wavelength of a typical particle:
$\lambda_T = \frac{h}{p} \sim \frac{h}{\left(2Mk_BT\right)^{1/2}}$
It is conventional to insert π.
Define λ_T = thermal wavelength $= \frac{h}{\left(2\pi Mk_BT\right)^{1/2}}$

Classical behaviour is seen if the particle spacing $d \sim \left(\frac{V}{N}\right)^{1/3} >> \lambda_T$ i.e. quantum effects are unimportant if the particle spacing is much greater than the de Broglie wavelength of a typical particle.

Define $n_Q = \frac{1}{\lambda_T^{\,3}}$ to be the quantum concentration.

The classical limit is when $n << n_Q$, i.e. at low densities.

So the classical limit is a low density, high temperature approximation.

NB: $\lambda_T \to \infty$ as $T \to 0$, so classical behaviour always fails at low temperature.

3.2 Single Particle Partition Function ζ

Particle function Z → free energy $F = -k_BT \ln Z$ → pressure, entropy, etc.

For one-particle in a box:
$\zeta = \sum_{all\ k\ states} e^{-\frac{\varepsilon(k)}{k_BT}}$
We can use the approximation
$\sum e^{-\frac{\varepsilon(k)}{k_BT}} \to \left(2s+1\right)\int_0^\infty \frac{Vk^2}{2\pi^2} dk e^{-\frac{\hbar^2k^2}{2Mk_BT}}$
where:
$\left(2s+1\right)$ is if the particles have spin. $s = 0$ for simplicity.

$$\frac{Vk^2}{2\pi^2}dk = \rho(k)dk$$

$e^{-\frac{\hbar^2 k^2}{2Mk_BT}}$ is the Boltzmann distribution.

$$\zeta = Vn_Q = \frac{V}{\lambda_T{}^3}$$

Integral is straightforward – very important.

$$I = \int_0^\infty e^{-\alpha x^2} x^2 dx$$

where α is the constants, and $x = k$.

$$I = -\frac{d}{d\alpha}\left(\int_0^\infty e^{-\alpha x^2} dx\right)$$

Set $y = \sqrt{\alpha}x$, so $dy = \sqrt{\alpha}dx$.

$$I = -\frac{d}{d\alpha}\left(\frac{1}{\sqrt{\alpha}}\int_0^\infty e^{-y^2} dy\right)$$

$\int_0^\infty e^{-y^2} dy = \frac{\sqrt{\pi}}{\alpha^{3/2}}$ (a well-known integral)

$$I = -\frac{d}{d\alpha}\left[\frac{\sqrt{\pi}}{2\sqrt{\alpha}}\right] = \frac{1}{4}\frac{\sqrt{\pi}}{\alpha^{3/2}}$$

In our integral, $\alpha = \frac{\hbar^2}{2Mk_BT}$ and $x = k$. So:

$$\zeta = \frac{V}{2\pi^2}\frac{\sqrt{\pi}}{4}\left[\frac{2Mk_BT}{\hbar^2}\right]^{3/2} = V\left(\frac{Mk_BT}{2\pi\hbar^2}\right)^{3/2} = \frac{V}{\lambda_T{}^3} = Vn_Q$$

$$\int_0^\infty e^{-y^2} dy = \frac{1}{2}\int_{-\infty}^\infty dy\, e^{-y^2}$$

$$J = \int_0^\infty dy\, e^{-y^2}$$

$$J^2 = \int_{-\infty}^\infty dy\, e^{-y^2}\int_{-\infty}^\infty dx\, e^{-x^2}$$

(x is the same as y …)

$$J^2 = \int_{-\infty}^\infty\int_{-\infty}^\infty dx\, dy\, e^{-\left(x^2+y^2\right)} = \int_0^\infty\int_0^{2\pi} r\, dr\, d\theta\, e^{-r^2}$$

$$= 2\pi\int_0^\infty dr\, r\, e^{-r^2} = 2\pi\left[-\frac{1}{2}e^{-r^2}\right]_0^\infty$$

$$= \pi$$

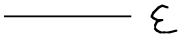
So $J = \sqrt{\pi}$.

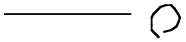
3.3 – N Particle Partition Function Z.
(M 7.1, B&S 6.5)

$Z = \sum e^{-E/k_B T}$

where the sum is over all the allowed microstates of the N particle system.
For distinguishable particles, $Z = 3^N$.
For indistinguishable particles, $Z \neq 3^N$.

Consider two spinless bosons each of which can be in two energy levels 0 and ϕ.





For one particle,

$\zeta = \sum e^{-E/K_B T} = e^{-0} + e^{-\varepsilon/k_B T} = 1 + e^{-\varepsilon/k_B T}$

Distinguishable:
Particles labeled a and b.
2 particle system has 4 microstates.
$(a,b) = (0,0)$, $(0,\varepsilon)$, $(\varepsilon,0)$ and $(\varepsilon,\varepsilon)$.
These have energies of 0, ε, ε and 2ε respectively.
The partition function is:

$Z = e^{-0} + 2e^{-\beta\varepsilon} + e^{-2\beta\varepsilon} = \left(1 + e^{-\beta\varepsilon}\right)^2 = \zeta^2$

Indistinguishable:
2 particle system has three microstates $(0,0)$, $(0,\varepsilon)$ and $(\varepsilon,\varepsilon)$. The case of $(\varepsilon,0)$ is dismissed as it is indistinguishable from $(0,\varepsilon)$.
Energies are 0, ε and 2ε.
The partition function is:

$Z = e^{-0} + e^{-\beta\varepsilon} + e^{-2\beta\varepsilon} = 1 + e^{-\beta\varepsilon} + e^{-2\beta\varepsilon} \neq \zeta^2$.

To prove:
For indistinguishable particles in the classical limit $d >> \lambda_T$ (or $n << n_Q = 1/\lambda_T{}^3$).

$Z \approx \frac{\zeta^N}{N!}$ where ζ the partition function is $= Vn_Q = \frac{V}{\lambda_T{}^3}$.

A typical particle in a classical gas has $\varepsilon \sim k_B T$. The probability of a state being occupied is equal to $\frac{e^{-\beta\varepsilon}}{\zeta} \sim \frac{e^{-1}}{\zeta} \sim \frac{1}{\zeta}$ for $\varepsilon \sim k_B T$.

For N particles in a box, the number of particles in a state $\sim \frac{N}{\zeta} = \frac{N}{Vn_Q} = \frac{n}{n_Q}$. But in the classical regime, $n << n_Q$, so $\frac{n}{n_Q} << 1$. Hence in the classical limit, there is a very low probability (negligible) of having more than one particle in any k state.
Accessible k states are more common than occupied states.

Each microstate for indistinguishable particles corresponds to $N!$ microstates for distinguishable particles. $N!$ is the number of arrangements of distinguishable particles. Therefore the sum of the allowed microstates $\sum e^{-E/k_BT}$ is reduced by a factor of $N!$ from that of distinguishable particles.
Therefore:
$Z = \dfrac{\left(Vn_Q\right)^N}{N!}$ in the classical limit.

3.4 Properties of the Classical Gas

a) *Helmholtz Free Energy F*
$F = -k_BT \ln Z$

b) *Internal energy*
$$E = +\frac{\partial}{\partial\beta}\left(\frac{F}{k_BT}\right) = \frac{\partial}{\partial\beta}(-\ln Z)$$
$$\ln Z = N\ln V + N\ln n_Q - \ln N!$$
$$n_Q \sim \frac{1}{\beta e^{3/2}},\ \beta = \frac{1}{k_BT}$$
$$\ln n_Q = -\frac{3}{2}\ln\beta$$
$$E = \frac{3}{2}N\frac{\partial\ln\beta}{\partial\beta} = \frac{3}{2}\frac{N}{\beta} = \frac{3}{2}Nk_BT$$
as expected from the equipartition function.

c) *Pressure*
$$P = -\left(\frac{\partial F}{\partial V}\right)_{N,T} = k_BTN\frac{\partial\ln V}{\partial V} = k_BT\frac{N}{V}$$
therefore $pV = Nk_BT$ the ideal gas law (in classical limits).
For one mole, $N = N_A$, $pV = RT$. $R = N_Ak_B$.

d) Entropy
$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N}$$
Use Sterling's Formula $\ln N! = N\ln N - N + ...$
$$S = Nk_B\left[\ln\left(\frac{V}{N}\right) + \frac{3}{2}\ln(T) + \frac{3}{2}\ln\left(\frac{Mk_B}{2\pi\hbar^2}\right) + \frac{5}{2}\right]$$
the Sackur-Tetrode equation.
NB: it gales at low T. Predicts $S \to -\infty$ as $T \to 0$. This is due to the failure of the classical approximation as $T \to 0$.
If we had included spin, there would have been an additional term in the entropy $Nk_B\ln(2s+1)$ where $2s+1$ is the spin degeneracy.

Disorder associated with the spins: 2^N arrangements of the N spins for $S = \frac{1}{2}$.

This is the only quantity affected by the spin degeneracy.

e) Chemical Potential

$$\mu = \left(\frac{\partial F}{\partial N} \right)_{V,T}$$

$$\mu = -\frac{3}{2} k_B T \ln \left(\frac{N}{V} \left(\frac{2\pi M k_B T}{h^2} \right)^{3/2} \right) = -\frac{3}{2} k_B T \ln \frac{d^2}{\lambda_T{}^2}$$

This is negative in the classical regime where $d >> \lambda_T$.

3.5 How good is the classical approximation at STP?

(STP = Standard Temperature and Pressure)

$p = \frac{N}{V} k_B T$, so $\frac{N}{V} \approx 3 \times 10^{25} m^{-3}$ at STP.

The typical distance between particles is $d \sim \left(\frac{V}{N} \right)^{1/3} = 3.2nm$

$$\lambda_T = \frac{h}{\left(2\pi M k_B T \right)^{1/2}} \sim 0.05nm$$

So $d > \lambda_T$, so the approximation is good. However it is still the same order of magnitude, so there are quantum effects present – very sensitive experiments can detect them. These effects become much larger at lower temperatures.