Ideal systems

System of free spins

Let us consider N particles with spin $\frac{1}{2}$:

$$\begin{array}{rcl} S_i & = & \frac{1}{2}\hbar \\ S_{iz} & = & \pm\frac{1}{2}\hbar \end{array} \qquad i = 1, \ldots, N.$$

The z component of the total spin is

$$S_z = \sum_i S_{iz} = \frac{1}{2}\hbar (N^+ - N^-),$$

where

$$\begin{array}{rcl} N^+ & = & +\frac{1}{2}\hbar \text{ spin count} \\ N^- & = & -\frac{1}{2}\hbar \text{ spin count.} \end{array}$$

S_z determines the macrostate of the system.
Denoting $S_z = \hbar\nu$ we have

$$\begin{array}{rcl} N^+ & = & \frac{1}{2}N + \nu \\ N^- & = & \frac{1}{2}N - \nu \end{array}$$

and

$$\nu = -\frac{1}{2}N, -\frac{1}{2}N + 1, \ldots, \frac{1}{2}N.$$

Let $W(\nu)$ the number of those microstates for which $S_z = \hbar\nu$, i.e. $W(\nu)$ tells us, how many ways there are to distribute N particles into groups of N^+ and N^- particles so that $N^+ + N^- = N$ and $N^+ - N^- = 2\nu$.
From combinatorics we know that

$$\begin{array}{rcl} W(\nu) & = & \left(\begin{array}{c} N \\ N^+ \end{array}\right) = \frac{N!}{N^+!N^-!} \\ & = & \frac{N!}{(\frac{1}{2}N + \nu)!(\frac{1}{2}N - \nu)!}. \end{array}$$

$W(\nu)$ the *degeneracy* of the state $S_z = \hbar\nu$.
The Boltzmann entropy is

$$S = k_B \ln W(\nu).$$

Using Stirling's formula

$$\ln N! \approx N \ln N - N$$

we get

$$\begin{array}{rcl} \ln W(\nu) & \approx & N \ln N - N \\ & & - \left[(\frac{1}{2}N + \nu)\ln(\frac{1}{2}N + \nu) - (\frac{1}{2}N + \nu)\right] \\ & & - \left[(\frac{1}{2}N - \nu)\ln(\frac{1}{2}N - \nu) - (\frac{1}{2}N - \nu)\right] \\ & = & \frac{1}{2}N \ln \frac{N^2}{\frac{1}{4}N^2 - \nu^2} - \nu \ln \frac{\frac{1}{2}N + \nu}{\frac{1}{2}N - \nu}. \end{array}$$

We look for the extremum of $W(\nu)$:

$$\begin{array}{rcl} \frac{\partial \ln W(\nu)}{\partial \nu} & = & \frac{1}{2}N \frac{\frac{1}{4}N^2 - \nu^2}{N^2} \frac{N^2}{\left(\frac{1}{4}N^2 - \nu^2\right)^2} 2\nu \\ & & - \ln \frac{\frac{1}{2}N + \nu}{\frac{1}{2}N - \nu} \\ & & -\nu \frac{\frac{1}{2}N - \nu}{\frac{1}{2}N + \nu} \frac{\frac{1}{2}N - \nu + \frac{1}{2}N + \nu}{\left(\frac{1}{2}N - \nu\right)^2} \\ & = & -\ln \frac{\frac{1}{2}N + \nu}{\frac{1}{2}N - \nu} = 0. \end{array}$$

We can see that $\nu = 0$.
Now

$$\begin{array}{rcl} \left.\frac{\partial^2 \ln W(\nu)}{\partial \nu^2}\right|_{\nu=0} & = & \left.\frac{N}{\frac{1}{4}N^2 - \nu^2}\right|_{\nu=0} \\ & = & -\frac{4}{N} < 0, \end{array}$$

so $\nu = 0$ is a maximum.
Let us expand $\ln W(\nu)$ as a Taylor series in the vicinity of its maximum:

$$\ln W(\nu) = \ln W(0) - \frac{2}{N}\nu^2 + \mathcal{O}(\nu^3),$$

so $W(\nu)$ obeys the normal distribution

$$W(\nu) \approx W(0) e^{-\frac{2}{N}\nu^2},$$

whose deviation is

$$\Delta\nu = \frac{1}{2}\sqrt{N}.$$

In this distribution

$$\ln W(0) \approx N \ln 2$$

or

$$W(0) \approx 2^N.$$

Total number of states

We have exactly

$$\begin{array}{rcl} W_{\text{tot}} & = & \sum_{N^+} \left(\begin{array}{c} N \\ N^+ \end{array}\right) = (1+1)^N \\ & = & 2^N. \end{array}$$

According to the previous treatment we can write approximatively

$$\begin{array}{rcl} W_{\text{tot}}^{\text{appr}} & \approx & \sum_{\nu} W(0) e^{-\frac{2}{N}\nu^2} \approx W(0) \int_{-\infty}^{\infty} d\nu\, e^{-\frac{2}{N}\nu^2} \\ & \approx & 2^N \sqrt{\frac{\pi}{2}N}. \end{array}$$

On the other hand we have

$$\begin{array}{rcl} \ln W_{\text{tot}}^{\text{appr}} & = & \overbrace{N \ln 2}^{\text{extensive}} + \overbrace{\frac{1}{2}\ln\left(\frac{\pi}{2}N\right)}^{\text{non extensive}} \\ & = & \ln W_{\text{tot}} + \text{non extensive} \end{array}$$

Energy
Let's put the system in the external magnetic field

$$\boldsymbol{B} = \mu_0 \boldsymbol{H},$$

where

$$\boldsymbol{H} = H\hat{z}$$

is the magnetizing field.
The potential energy is

$$E = -\mu_0 \sum_i \boldsymbol{\mu}_i \cdot \boldsymbol{H} = -\mu_0 H \sum_i \mu_{iz},$$

where $\boldsymbol{\mu}_i$ is the magnetic moment of the particle i.
Now

$$\boldsymbol{\mu} = \gamma \boldsymbol{S},$$

where γ is the gyromagnetic ratio. For electrons we have

$$\gamma = 2\gamma_0 = -\frac{e}{m},$$

where γ_0 is the classical value $\frac{e}{2m}$.
For electrons we can further write

$$\mu_z^{\mathrm{e}} = -\mu_B \sigma_z = \mp \mu_B.$$

Here σ_z is the Pauli spin matrix and

$$\mu_B = \frac{e\hbar}{2m} = 5.79 \cdot 10^{-5} \frac{\mathrm{eV}}{\mathrm{T}}$$

the Bohr magneton.
Thus the energy is

$$E = -\mu_0 H \sum \mu_{iz} = -\mu_0 \gamma H S_z = \epsilon \nu,$$

where

$$\epsilon = -\hbar \gamma \mu_0 H$$

is the energy/particle. For electrons we have

$$\epsilon = 2\mu_0 \mu_B H.$$

Now

$$\Delta E = \epsilon \, \Delta \nu,$$

so from the condition

$$\omega(E) \, \Delta E = W(\nu) \, \Delta \nu$$

we get as the density of states

$$\omega(E) = \frac{1}{|\epsilon|} W\left(\frac{E}{\epsilon}\right).$$

1) Microcanonical ensemble
Denoting

$$E_0 = \frac{1}{2} \epsilon N,$$

the total energy will lie between $-E_0 \le E \le E_0$.
With the help of the energy the degeneracy can be written as

$$\begin{aligned} \ln W(\nu) &= \frac{1}{2} N \ln \frac{4E_0^2}{E_0^2 - E^2} - \frac{E}{\epsilon} \ln \frac{E_0 + E}{E_0 - E} \\ &= \ln \omega(E) + \ln |\epsilon|. \end{aligned}$$

As the entropy we get

$$\begin{aligned} S(E) &= k_B \ln \omega(E) \\ &= N k_B \left[\frac{1}{2} \ln \frac{4E_0^2}{E_0^2 - E^2} - \frac{E}{2E_0} \ln \frac{E_0 + E}{E_0 - E} \right] \\ &\quad + \text{non extensive term.} \end{aligned}$$

The temperature was defined like

$$\frac{1}{T} = \frac{\partial S}{\partial E},$$

so

$$\beta(E) = \frac{1}{k_B T(E)} = -\frac{N}{2E_0} \ln \frac{E_0 + E}{E_0 - E}.$$

We can solve for the energy:

$$\begin{aligned} E &= -E_0 \tanh \frac{\beta E_0}{N} \\ &= -\frac{1}{2} N \mu_0 \hbar \gamma H \tanh \left(\frac{\mu_0 \hbar \gamma H}{2k_B T} \right). \end{aligned}$$

The *magnetization* or the *magnetic polarization* means the magnetic moment per the volume element, i.e.

$$\boldsymbol{M} = \frac{1}{V} \sum_i \boldsymbol{\mu}_i.$$

The z component of the magnetization is

$$\begin{aligned} M_z &= -\frac{1}{V} \frac{\epsilon \nu}{\mu_0 H} = \frac{1}{V} \frac{\hbar \gamma \mu_0 H \nu}{\mu_0 H} \\ &= \frac{1}{V} \gamma \hbar \nu. \end{aligned}$$

Now

$$E = -\mu_0 H V M_z,$$

so we get for our system as the equation of state

$$M = \frac{1}{2} \rho \hbar \gamma \tanh \left(\frac{\mu_0 \hbar \gamma H}{2k_B T} \right),$$

where $\rho = N/V$ is the particle density.
Note The relations derived above

$$\begin{aligned} E &= E(T, H, N) \\ M &= M(T, H, N) \end{aligned}$$

determine the thermodynamics of the system.

2) Canonical ensemble
The canonical partition function is

$$Z = \sum_n e^{-\beta E_n}.$$

Here

$$E_n = -\mu_0 H \sum_{i=1}^{N} \mu_{iz}$$

the energy of a single microstate.
Denote

$$\mu_{iz} = \hbar \gamma \nu_i, \quad \nu_i = \pm \frac{1}{2}.$$

Now

$$\begin{aligned}
Z &= \sum_{\text{all microstates}} e^{\beta\mu_0 H \sum_i \mu_{iz}} \\
&= \sum_{\nu_1=-\frac{1}{2}}^{\frac{1}{2}} \cdots \sum_{\nu_N=-\frac{1}{2}}^{\frac{1}{2}} e^{\beta\mu_0\hbar\gamma H \sum_i \nu_i} \\
&= \left[\sum_{\nu=-\frac{1}{2}}^{\frac{1}{2}} e^{\beta\mu_0 H\gamma\hbar\nu}\right]^N = Z_1^N,
\end{aligned}$$

where Z_1 the one particle state sum

$$\begin{aligned}
Z_1 &= e^{-\frac{1}{2}\beta\mu_0 H\gamma} + e^{\frac{1}{2}\beta\mu_0 H\gamma} \\
&= 2\cosh\frac{\mu_0 H\gamma}{2k_B T}.
\end{aligned}$$

The same result can be obtained using the degeneracy:

$$\begin{aligned}
Z &= \sum_\nu W(\nu) e^{-\beta E(\nu)} \\
&= \sum_\nu W(\nu) e^{-\beta\epsilon\nu} \\
&= \sum_{N^+} \left(\begin{array}{c} N \\ N^+ \end{array}\right) e^{-\beta\epsilon(N^+ - \frac{1}{2}N)} \\
&= e^{-\frac{1}{2}\beta\epsilon N}\left(1 + e^{-\beta\epsilon}\right)^N.
\end{aligned}$$

The free energy F is

$$\begin{aligned}
F &= F(T, \boldsymbol{H}) = -k_B T \ln Z \\
&= -k_B T N \left[\ln 2 + \ln\cosh\frac{\mu_0 H\gamma\hbar}{2k_B T}\right].
\end{aligned}$$

The entropy is

$$\begin{aligned}
S &= -\left(\frac{\partial F}{\partial T}\right)_{\boldsymbol{H}} \\
&= N k_B \Bigg[\ln 2 + \ln\cosh\frac{\mu_0 H\gamma\hbar}{2k_B T} \\
&\qquad - \frac{\mu_0\hbar\gamma H}{2k_B T}\tanh\frac{\mu_0\hbar\gamma H}{2k_B T}\Bigg].
\end{aligned}$$

Differentiating the free energy with respect to the field $\boldsymbol{H}$ we get

$$\begin{aligned}
-\left(\frac{\partial F}{\partial H_z}\right)_T &= k_B T\frac{1}{Z}\frac{\partial}{\partial H}\sum_\nu W(\nu) e^{-\beta\epsilon\nu} \\
&= \mu_0\gamma\hbar\frac{1}{Z}\sum_\nu \nu W(\nu) e^{-\beta\epsilon\nu} \\
&= \mu_0\gamma\hbar\langle\nu\rangle = \mu_0 V M_z.
\end{aligned}$$

Thus the differential of the free energy is

$$dF = -S\,dT - \mu_0 V \boldsymbol{M}\cdot d\boldsymbol{H},$$

so the magnetization is

$$\begin{aligned}
M &= -\frac{1}{\mu_0 V}\left(\frac{\partial F}{\partial H}\right)_T \\
&= -\frac{1}{2}\rho\hbar\gamma\tanh\left(\frac{\mu_0\hbar\gamma H}{2k_B T}\right).
\end{aligned}$$

This is identical with the result we obtained in the microcanonical ensemble.
Also, the microcanonical entropy = the canonical entropy + a non extensive term.

Energy
a)

$$\begin{aligned}
E &= \langle E(\nu)\rangle = \epsilon\bar{\nu} = -\frac{1}{Z}\frac{\partial}{\partial\beta}Z \\
&= -\frac{1}{2}N\epsilon\tanh\left(\frac{1}{2}\beta\epsilon\right) \\
&= \text{the energy of the microcanonical enesmble.}
\end{aligned}$$

b) According to thermodynamics

$$F = E - TS$$

or

$$\begin{aligned}
E &= F + TS = F - T\frac{\partial F}{\partial T} \\
&= F + \beta\frac{\partial F}{\partial\beta} = \frac{\partial}{\partial\beta}(\beta F) \\
&= -\frac{\partial}{\partial\beta}\ln Z \\
&= \text{the energy given at } a).
\end{aligned}$$

Susceptibility
According to the definition the susceptibility is

$$\begin{aligned}
\chi &= \left(\frac{\partial M}{\partial H}\right)_T = -\frac{1}{\mu_0 V}\left(\frac{\partial^2 F}{\partial H^2}\right) \\
&= \frac{\mu_0\rho}{k_B T}\frac{\left(\frac{1}{2}\hbar\gamma\right)^2}{\cosh^2\left(\frac{\hbar\gamma\mu_0 H}{2K_B T}\right)}.
\end{aligned}$$

When $H \to 0$ we end up with *Curie's law*

$$\chi = \frac{C}{T},$$

where

$$C = \frac{\mu_0\rho}{k_B T}\left(\frac{1}{2}\hbar\gamma\right)^2.$$

Thermodynamical identifications
Earlier we identified

$$E^{\text{stat}} \equiv E = \langle H\rangle = U^{\text{term}} = \text{internal energy},$$

so

$$\begin{aligned}
F &= E - TS = F^{\text{therm}} \\
&= \text{the Helmholtz free energy} \\
&= U - TS.
\end{aligned}$$

Now

$$\begin{aligned}
dF &= -S\,dT - \mu_0 V\boldsymbol{M}\cdot d\boldsymbol{H} \\
&= dF^{\text{therm}} = -S\,dT - đW,
\end{aligned}$$

so

$$đW = \mu_0 V \boldsymbol{M}\cdot d\boldsymbol{H}.$$

Another possibility
Let us identify

$$E = \text{enthalpy} = H^{\text{therm}} = H.$$

Then

$$\begin{aligned} F &= E - TS = H^{\text{therm}} - TS = G^{\text{therm}} \\ &= \text{the Gibbs free energy} = G \end{aligned}$$

and

$$\begin{aligned} dG &= -S\,dT - \mu_0 V \boldsymbol{M}\cdot d\boldsymbol{H} \\ dH &= T\,dS - \mu_0 V \boldsymbol{M}\cdot d\boldsymbol{H}, \end{aligned}$$

so

$$\begin{aligned} G &= G(T, \boldsymbol{H}) \\ H &= H(S, \boldsymbol{H}). \end{aligned}$$

In the thermodynamics we had for a pVT system

$$dH = T\,dS + V\,dp,$$

from which we get the analogies

$$\begin{aligned} p &\longleftrightarrow -\mu_0 \boldsymbol{H} \quad \text{(intensive)} \\ V &\longleftrightarrow V\boldsymbol{M} \quad \text{(extensive)}. \end{aligned}$$

On the other hand we had

$$U = H - pV$$

and

$$dU = T\,dS - p\,dV = T\,dS - đW,$$

so now

$$U = H + \mu_0 V \boldsymbol{M}\cdot\boldsymbol{H}$$

and

$$dU = T\,dS + \mu_0 V \boldsymbol{H}\cdot d\boldsymbol{M},$$

fro which

$$đW = -\mu_0 V \boldsymbol{H}\cdot d\boldsymbol{M}.$$

Example *Adiabatic demagnetization* Now

$$\frac{S}{Nk_B} = \ln 2 + \ln\cosh x - x\tanh x,$$

where

$$x = \frac{\mu_0 \hbar H \gamma}{2k_B T}.$$

When $T \to 0$, then $x \to \infty$, so that

$$\begin{aligned} \ln\cosh x &= \ln \frac{1}{2} e^{x}(1 + e^{-2x}) \\ &= x - \ln 2 + e^{-2x} + \cdots \end{aligned}$$

and

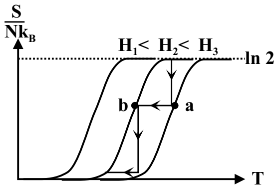
$$\begin{aligned} \tanh x &= \frac{e^{x}(1 - e^{-2x})}{e^{x}(1 + e^{-2x})} \\ &= 1 - 2e^{-2x} + \cdots. \end{aligned}$$

Hence

$$\frac{S}{Nk_B} \to 2xe^{-2x} + \cdots.$$

When $T \to \infty$, then $x \to 0$, and

$$\frac{S}{Nk_B} \to \ln 2.$$



We decrease the field adiabatically within the interval $a \to b$. Now $S = S(H/T)$, so that

$$S_a = S\left(\frac{H_a}{T_a}\right) = S_b = S\left(\frac{H_b}{T_b}\right)$$

or

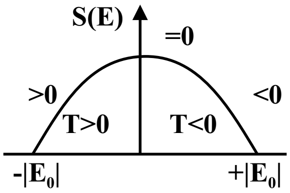
$$\frac{T_b}{T_a} = \frac{H_b}{H_a}.$$

Negative temperature
The entropy of the spin system is

$$S(E) = Nk_B\left[\frac{1}{2}\ln\frac{4E_0^2}{E_0^2 - E^2} - \frac{E}{2E_0}\ln\frac{E_0 + E}{E_0 - E}\right],$$

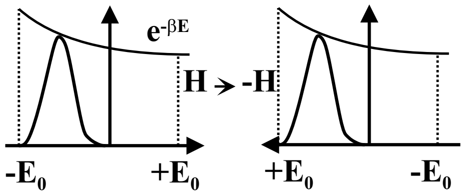
where

$$E_0 = \mu_0 \mu_B H N \text{ ja } -|E_0| < E < |E_0|.$$



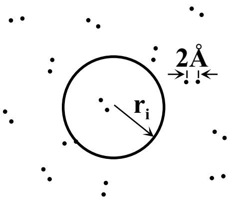
Now

$$\beta(E) = \frac{1}{k_B}\frac{\partial S}{\partial E} = -\frac{N}{2E_0}\ln\frac{E + E_0}{E - E_0}.$$



Originally the maximum of $\omega(E)e^{-\beta E}/Z$ is at a negative value E. Reversing the magnetic field abruptly $E \to -E$ and correspondingly $\beta \to -\beta$.
The temperature can be negative if the energy is bounded both above and below.

Classical ideal gas (Maxwell-Boltzmann gas)



We define r_i so that

$$\text{The volume occupied by one molecule} = v_i = \frac{4}{3}\pi r_i^3 = \frac{V}{N} = \frac{1}{\rho}$$

or

$$r_i = \sqrt[3]{\frac{3}{4\pi\rho}}.$$

Typically

- the diameter of an atom or a molecule $d \approx 2$Å.
- the range of the interaction 2–4Å.
- the free path (collision interval) $l \approx 600$Å.
- at STP ($T = 273$K, $p = 1$atm) $r_i \approx 20$Å.

or

$$\begin{array}{ccccc} d & \ll & r_i & \ll & l \\ 2 & & 20 & & 600 \quad \text{Å} \end{array}$$

The most important effect of collisions is that the system *thermalizes* i.e. attains an equilibrium, which corresponds to a statistical ensemble. Otherwise we can forget the collisions.

Let us consider a system of *one molecule* which can exchange energy (heat) with its surroundings. Then the suitable ensemble is the canonical ensemble and the distribution the Boltzmann distribution

$$\rho_l = \langle l|\,\rho\,|l\rangle = \frac{1}{Z}\,e^{-\beta\epsilon_l},$$

where the canonical partition function is

$$Z = \sum_l e^{-\beta\epsilon_l}.$$

Since in the k-space the density of 1 particle states is constant, in the *velocity space*, where

$$d^3v = \frac{1}{m^3}\,d^3p = \left(\frac{\hbar}{m}\right)^3 d^3k,$$

the density of states is also constant.

Because the system is translationally invariant we have

$$\epsilon_k = \langle \boldsymbol{k}|\,H\,|\boldsymbol{k}\rangle = \frac{\hbar^2k^2}{2m} = \frac{1}{2}mv^2,$$

so that the velocity distribution is

$$f(\boldsymbol{v}) \propto \langle \boldsymbol{k}|\,\rho\,|\boldsymbol{k}\rangle = e^{-\frac{mv^2}{2k_BT}}$$

or

$$f(\boldsymbol{v}) = Ce^{-\frac{mv^2}{2k_BT}}.$$

C can be determined from the condition

$$\begin{aligned} 1 &= \int f(\boldsymbol{v})\,d^3v = C\left[\int_{-\infty}^{\infty} dv_x e^{-\frac{mv_x^2}{2k_BT}}\right]^3 \\ &= C\left(\frac{2\pi k_BT}{m}\right)^{3/2}. \end{aligned}$$

Thus the velocity obeys *Maxwell's distribution*

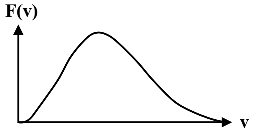
$$f(\boldsymbol{v}) = \left(\frac{m}{2\pi k_BT}\right)^{3/2} e^{-\frac{mv^2}{2k_BT}}.$$

From the relation

$$\int d^3v = \int_0^\infty 4\pi v^2 dv$$

we can obtain for the *speed* (the absolute value of the velocity $v = |\boldsymbol{v}|$) the distribution $F(v)$

$$F(v) = 4\pi v^2 f(v).$$



- The most probable speed

$$v_m = \sqrt{\frac{2k_BT}{m}}.$$

- The average of the speed

$$\langle v\rangle = \int_0^\infty dv\,vF(v) = \sqrt{\frac{8k_BT}{\pi m}}.$$

- The average of the square of the speed

$$\langle v^2\rangle = \int_0^\infty dv\,v^2F(v) = \frac{3k_BT}{m}.$$

Note

$$\left\langle \frac{1}{2}mv_x^2\right\rangle = \left\langle \frac{1}{2}mv_y^2\right\rangle = \left\langle \frac{1}{2}mv_z^2\right\rangle = \frac{1}{2}k_BT$$

and

$$\left\langle \frac{1}{2}mv^2\right\rangle = 3\left\langle \frac{1}{2}mv_x^2\right\rangle = \frac{3}{2}k_BT,$$

i.e. the energy is evenly distributed among the 3 (translational) degrees of freedom: the *equipartition* of the energy.

Partition function and thermodynamics

The single particle partition function is

$$\begin{aligned} Z_1(\beta) &= \int dE\,\omega(E)e^{-\beta E} \\ &= g\sum_{\boldsymbol{k}} e^{-\beta\frac{\hbar^2k^2}{2m}} = g\,\frac{V}{h^3}\int d^3p\,e^{-\frac{p^2}{2mk_BT}} \\ &= g\,\frac{V}{h^3}\,(2\pi mk_BT)^{3/2}. \end{aligned}$$

Here g is the spin degeneracy.
When we denote the *thermal de Broglie wave length* by

$$\lambda_T = \sqrt{\frac{h^2}{2\pi m k_B T}}$$

we can write the 1 body partition function as

$$Z_1(\beta) = g\,\frac{V}{\lambda_T^3}.$$

In the N particle system the canonical partition function takes the form

$$\begin{aligned} Z_N &= \frac{1}{N!}\,g^N \sum_{\boldsymbol{k}_1}\cdots\sum_{\boldsymbol{k}_N} e^{-\beta(\epsilon_{\boldsymbol{k}_1}+\cdots+\epsilon_{\boldsymbol{k}_1})} \\ &= \frac{1}{N!}\,g^N \left(\sum_{\boldsymbol{k}} e^{-\beta\epsilon_{\boldsymbol{k}}}\right)^N \\ &= \frac{1}{N!}\,Z_1^N. \end{aligned}$$

Here $N!$ takes care of the fact that each state

$$|\boldsymbol{k}_1,\ldots,\boldsymbol{k}_N\rangle$$

is counted only once. Neither the multiple occupation nor the Pauli exclusion principle has been taken into account. Using Stirling's formula $\ln N! \approx N\ln N - N$ the free energy can be written as

$$\begin{aligned} F_N &= \\ &= -k_BT\ln Z_N \\ &= Nk_BT\left[\ln\frac{N}{V} - 1 - \ln g + h\lambda_T^3\right] \\ &= Nk_BT\left[\ln\frac{N}{V} - \frac{3}{2}\ln T - 1 - \ln g + \frac{3}{2}\ln\frac{h^2}{2\pi m k_B}\right]. \end{aligned}$$

Since

$$dF = -S\,dT - p\,dV + \mu\,dN,$$

the pressure will be

$$p = -\frac{\partial F}{\partial V} = Nk_BT\,\frac{1}{V}$$

i.e. we end up with the *ideal gas equation of state*

$$pV = Nk_BT.$$

With the help of the entropy

$$S = -\frac{\partial F}{\partial T} = -\frac{F}{T} + \frac{3}{2}Nk_B$$

the internal energy is

$$U = F + TS = \frac{3}{2}Nk_BT$$

i.e. the *ideal gas internal energy.*

The heat capacity is

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{V,N} = \frac{3}{2}Nk_B.$$

Comparing this with

$$C_V = \frac{1}{2}fk_BN$$

we see that the number of degrees of freedom is $f = 3$.

Grand canonical partition function
According to the definition we have

$$Z_{\mathrm{G}} = \sum_N\sum_n e^{-\beta(E_n^{(N)}-\mu N)} = \sum_N z^N Z_N,$$

where

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

is called the *fugacity* and Z_N is the partition function of N particles.
So we get

$$\begin{aligned} Z_{\mathrm{G}} &= \sum_N \frac{1}{N!}\,z^N Z_1^N = e^{zZ_1} \\ &= \exp\left[e^{\beta\mu}\frac{gV}{\lambda_T^3}\right]. \end{aligned}$$

The grand potential is

$$\Omega(T,V,\mu) = -k_BT\ln Z_{\mathrm{G}} = -k_BTe^{\beta\mu}\frac{gV}{\lambda_T^3}.$$

Since

$$d\Omega = -S\,dT - p\,dV - \bar{N}\,d\mu,$$

we get

$$p = -\frac{\partial\Omega}{\partial V} = -\frac{\Omega}{V} = k_BTe^{\beta\mu}\frac{g}{\lambda_T^3}$$

and

$$\bar{N} = -\frac{\partial\Omega}{\partial\mu} = e^{\beta\mu}\frac{gV}{\lambda_T^3} = \frac{pV}{k_BT}$$

or we end up with the *ideal gas equation of state*

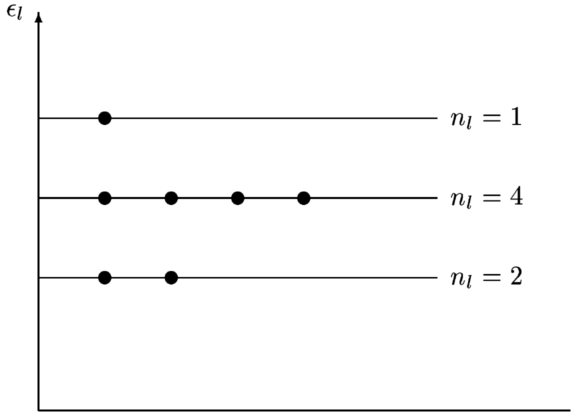
$$pV = \bar{N}k_BT.$$

Here

$$\begin{aligned} \bar{N} &= \langle N\rangle = \frac{\sum_N Nz^NZ_N}{\sum_N z^NZ_N} \\ &= \frac{1}{Z_{\mathrm{G}}}\,z\,\frac{\partial Z_{\mathrm{G}}}{\partial z} = \frac{\partial\ln Z_{\mathrm{G}}}{\partial\ln z}. \end{aligned}$$

Another way

We distribute N particles among the 1 particle states so that in the state l there are n_l particles.



Now

$$N = \sum_l n_l \text{ and } E = \sum_l \epsilon_l n_l.$$

The number of possible distributions is

$$W = W(n_1, n_2, \ldots, n_l, \ldots) = \frac{N!}{n_1! n_2! \cdots n_l! \cdots}.$$

Since in every distribution $(n_1, n_2, \ldots)$ everyone of the $N!$ permutatations of the particles gives an identical state the partition function is

$$\begin{aligned}
Z_{\mathrm{G}} &= \operatorname{Tr} e^{-\beta(H-\mu\hat{N})} \\
&= \sum_{n_1=0}^{\infty}\sum_{n_2=0}^{\infty}\cdots \frac{1}{N!} W e^{-\beta(E-\mu N)} \\
&= \sum_{n_1=0}^{\infty}\sum_{n_2=0}^{\infty}\cdots \frac{1}{n_1! n_2! \cdots} e^{-\beta\sum_l n_l(\epsilon_l-\mu)} \\
&= \prod_l \left[\sum_{n=0}^{\infty} \frac{1}{n!} e^{-\beta n(\epsilon_l-\mu)}\right] \\
&= \prod_l \exp\left[e^{-\beta(\epsilon_l-\mu)}\right] \\
&= \exp\left[\sum_l e^{-\beta(\epsilon_l-\mu)}\right] \\
&= \exp\left[e^{\beta\mu} Z_1\right]
\end{aligned}$$

or exactly as earlier.
Now

$$\begin{aligned}
\frac{\partial \ln Z_{\mathrm{G}}}{\partial \epsilon_l} &= \frac{-\beta\sum_{n=0}^{\infty} n \frac{1}{n!} e^{-\beta n(\epsilon_l-\mu)}}{\prod_l \left[\sum_{n=0}^{\infty} \frac{1}{n!} e^{-\beta n(\epsilon_l-\mu)}\right]} \\
&= -\beta \langle n_l \rangle
\end{aligned}$$

so the *occupation number* $\bar{n}_l$ of the state l is

$$\begin{aligned}
\bar{n}_l &= \langle n_l \rangle = -\frac{1}{\beta}\frac{\partial \ln Z_{\mathrm{G}}}{\partial \epsilon_l} = -\frac{1}{\beta}\frac{\partial}{\partial \epsilon_l} e^{-\beta(\epsilon_l-\mu)} \\
&= e^{-\beta(\epsilon_l-\mu)}.
\end{aligned}$$

The Boltzmann distribution gives a wrong result if the 1 particle states are multiply occupied. Our approximation is therefore valid only if

$$\bar{n}_l \ll 1 \quad \forall l$$

or

$$e^{\beta\mu} \ll e^{\beta\epsilon_l} \quad \forall l.$$

Now $\min \epsilon_l = 0$, so that

$$e^{\beta\mu} \ll 1.$$

On the other hand

$$e^{\beta\mu} = \frac{\bar{N}}{V}\lambda_T^3, \text{ when } g = 1$$

and

$$\frac{\bar{N}}{V} = \frac{1}{v_i} = \frac{3}{4\pi r_i^3},$$

so we must have

$$\lambda_T \ll r_i.$$

Now

$$\lambda_T = \sqrt{\frac{h^2}{2\pi m k_B T}}$$

is the minimum diameter of the wave packet of a particle with the typical thermal energy ($\bar{\epsilon}_l = k_B T$) so in other words:
The Maxwell-Boltzmann approximation is valid when the wave packets of individual particles do not overlap.

Occupation number representation

Let us consider a system of N non interacting particles. Denote by

$$|n_1, n_2, \ldots, n_i, \ldots\rangle$$

the quantum state where there are n_i particles in the 1 particle state i. Let the energy of the state i be ϵ_i. Then

$$\begin{aligned}
H|n_1, n_2, \ldots\rangle &= \left(\sum_i n_i\epsilon_i\right)|n_1, n_2, \ldots\rangle \\
N &= \sum_i n_i.
\end{aligned}$$

We define the *creation operator* $a_i^\dagger$ so that

$$a_i^\dagger |n_1, n_2, \ldots, n_i, \ldots\rangle = C|n_1, n_2, \ldots, n_i + 1, \ldots\rangle$$

i.e. $a_i^\dagger$ creates one particle into the state i.
Correspondingly the *destruction operator* a_i obeys:

$$a_i |n_1, n_2, \ldots, n_i, \ldots\rangle = C'|n_1, n_2, \ldots, n_i - 1, \ldots\rangle,$$

i.e. a_i removes one particle from the state i.
The basis $\{|n_1, n_2, \ldots\rangle\}$ is complete, i.e.

$$\sum_{\{n_i\}} |n_1, n_2, \ldots\rangle\langle n_1, n_2, \ldots| = 1$$

and orthonormal or

$$\langle n_1', n_2', \ldots \mid n_1, n_2, \ldots \rangle = \delta_{n_1 n_1'} \delta_{n_2 n_2'} \cdots .$$

Bosons
For bosons the creation and destruction operators obey the commutation relations

$$\begin{aligned} [a_i, a_j^\dagger] &= \delta_{ij} \\ [a_i, a_j] &= [a_i^\dagger, a_j^\dagger] = 0. \end{aligned}$$

It can be shown that

$$\begin{aligned} a_i \left| n_1, \ldots, n_i, \ldots \right\rangle &= \sqrt{n_i} \left| n_1, \ldots, n_i - 1, \ldots \right\rangle \\ a_i^\dagger \left| n_1, \ldots, n_i, \ldots \right\rangle &= \sqrt{n_i + 1} \left| n_1, \ldots, n_i + 1, \ldots \right\rangle . \end{aligned}$$

The *(occupation) number operator*

$$\hat{n}_i = a_i^\dagger a_i$$

obeys the relation

$$\begin{aligned} \hat{n}_i \left| n_1, \ldots, n_i, \ldots \right\rangle &= a_i^\dagger a_i \left| n_1, \ldots, n_i, \ldots \right\rangle \\ &= n_i \left| n_1, \ldots, n_i, \ldots \right\rangle \end{aligned}$$

and $n_i = 0, 1, 2, \ldots$.
An arbitrary one particle operator, i.e. an operator $O^{(1)}$, which in the configuration space operates only on the coordinates on one particle, can be written in the occupation number representation as

$$\hat{O}^{(1)} = \sum_{i,j} \left\langle i \middle| O^{(1)} \middle| j \right\rangle a_i^\dagger a_j .$$

A two body operator $O^{(2)}$ can be written as

$$\hat{O}^{(2)} = \sum_{ijkl} \left\langle ij \middle| O^{(2)} \middle| kl \right\rangle a_i^\dagger a_j^\dagger a_l a_k .$$

Example Hamiltonian

$$H = \sum_i -\frac{\hbar^2}{2m} \nabla_i^2 + \frac{1}{2} \sum_{i \neq j} V(\boldsymbol{r}_i, \boldsymbol{r}_j)$$

takes in the occupation representation the form

$$\begin{aligned} H &= \sum_{i,j} \left\langle i \middle| -\frac{\hbar^2}{2m} \nabla^2 \middle| j \right\rangle a_i^\dagger a_j \\ &\quad + \frac{1}{2} \sum_{ijkl} \left\langle ij \right| V \left| kl \right\rangle a_i^\dagger a_j^\dagger a_l a_k , \end{aligned}$$

where

$$\left\langle i \middle| -\frac{\hbar^2}{2m} \nabla^2 \middle| j \right\rangle = -\frac{\hbar^2}{2m} \phi_i^*(\boldsymbol{r}) \nabla^2 \phi_j(\boldsymbol{r}) \, d^3 r$$

and

$$\begin{aligned} &\left\langle ij \right| V \left| kl \right\rangle = \\ &\quad \int \phi_i^*(\boldsymbol{r}_1) \phi_j^*(\boldsymbol{r}_2) V(\boldsymbol{r}_1, \boldsymbol{r}_2) \phi_k(\boldsymbol{r}_2) \phi_l(\boldsymbol{r}_1) \, d^3 r_1 \, d^3 r_2 . \end{aligned}$$

Fermions
The creation and destruction operators of fermions satisfy the *anti*commutation relations

$$\begin{aligned} \{a_i, a_j^\dagger\} &= a_i a_j^\dagger + a_j^\dagger a_i = \delta_{ij} \\ \{a_i, a_j\} &= \{a_i^\dagger, a_j^\dagger\} = 0. \end{aligned}$$

It can be shown that

$$\begin{aligned} &a_i \left| n_1, \ldots, n_i, \ldots \right\rangle = \\ &\quad \begin{cases} (-1)^{S_i} \sqrt{n_i} \left| n_1, \ldots, n_i - 1, \ldots \right\rangle , & \text{if } n_i = 1 \\ 0, & \text{otherwise} \end{cases} \\ &a_i^\dagger \left| n_1, \ldots, n_i, \ldots \right\rangle = \\ &\quad \begin{cases} (-1)^{S_i} \sqrt{n_i + 1} \left| n_1, \ldots, n_i + 1, \ldots \right\rangle , & \text{if } n_i = 0 \\ 0, & \text{otherwise} \end{cases} \end{aligned}$$

Here

$$S_i = n_1 + n_2 + \cdots + n_{i-1} .$$

The number operator satisfies

$$\hat{n}_i \left| n_1, \ldots, n_i, \ldots \right\rangle = n_i \left| n_1, \ldots, n_i, \ldots \right\rangle$$

and $n_i = 0, 1$.
One and two body operators take the same form as in the case of bosons.
Note Since a_i and a_j *anticommute* one must be careful with the order of the creation and destruction operators in $O^{(2)}$.
In the case of non interacting particles the Hamiltonian operator in the configuration space is

$$H = \sum_i H_1(\boldsymbol{r}_i),$$

where 1 body Hamiltonian H_1 is

$$H_1(\boldsymbol{r}_i) = -\frac{\hbar^2}{2m} \nabla_i^2 + U(\boldsymbol{r}_i).$$

Let ϕ_j be eigenfunctions of H_1 i.e.

$$H_1 \phi_j(\boldsymbol{r}) = \epsilon_j \phi(\boldsymbol{r}).$$

In the occupation space we have then

$$\hat{H} = \sum_j \epsilon_j a_j^\dagger a_j = \sum_j \epsilon_j \hat{n}_j$$

and

$$\hat{N} = \sum_j a_j^\dagger a_j = \sum_j \hat{n}_j .$$

The grand canonical partition function is now

$$Z_{\mathrm{G}} = \operatorname{Tr} e^{-\beta(\hat{H} - \mu \hat{N})} = \sum_{n_1} \sum_{n_2} \cdots e^{-\beta \sum_l n_l (\epsilon_l - \mu)} .$$

Bose-Einstein ideal gas

In bosonic systems the occupations of one particle states are $n_l = 0, 1, 2, \ldots$. The grand canonical state sum is

$$\begin{aligned} Z_{\mathrm{G,BE}} &= \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \cdots e^{-\beta \sum_l n_l(\epsilon_l-\mu)} \\ &= \prod_l \left[\sum_{n=0}^{\infty} e^{-\beta n(\epsilon_l-\mu)} \right] \\ &= \prod_l \frac{1}{1-e^{-\beta(\epsilon_l-\mu)}}. \end{aligned}$$

The grand potential is

$$\Omega_{\mathrm{BE}} = k_B T \sum_l \ln\left[1-e^{-\beta(\epsilon_l-\mu)}\right].$$

The occupation number of the state l is

$$\begin{aligned} \bar{n}_l &= \langle n_l \rangle = \frac{1}{Z_{\mathrm{G}}} \sum_{n_1}\sum_{n_2} \cdots n_l e^{-\beta \sum_m n_m(\epsilon_m-\mu)} \\ &= -\frac{1}{\beta}\frac{\partial}{\partial \epsilon_l} \ln Z_{\mathrm{G}} = \frac{\partial \Omega}{\partial \epsilon_l}, \end{aligned}$$

and for the *Bose-Einstein occupation number* we get

$$\bar{n}_l = \frac{1}{e^{\beta(\epsilon_l-\mu)}-1}.$$

Entropy

Since $d\Omega = -S\,dT - p\,dV - N\,d\mu$ we have

$$\begin{aligned} S &= \left(\frac{\partial \Omega}{\partial T}\right)_\mu \\ &= -k_B \sum_l \ln\left[1-e^{-\beta(\epsilon_l-\mu)}\right] \\ &\quad -k_B T \sum_l \frac{1}{1-e^{-\beta(\epsilon_l-\mu)}} (\epsilon_l-\mu) e^{-\beta(\epsilon_l-\mu)} \frac{-1}{k_B T^2}. \end{aligned}$$

Now

$$e^{\beta(\epsilon_l-\mu)} = 1 + \frac{1}{\bar{n}_l}$$

and

$$\beta(\epsilon_l-\mu) = \ln(1+\bar{n}_l) - \ln \bar{n}_l,$$

so

$$\begin{aligned} S &= -k_B \sum_l \ln\left(1-\frac{\bar{n}_l}{\bar{n}_l+1}\right) \\ &\quad +k_B \sum_l \bar{n}_l \left[\ln(\bar{n}_l+1) - \ln \bar{n}_l\right] \end{aligned}$$

or

$$S = k_B \sum_l \left[(\bar{n}_l+1)\ln(\bar{n}_l+1) - \bar{n}_l \ln \bar{n}_l\right].$$

Fermi-Dirac ideal gas

The Hamiltonian operator is

$$\hat{H} = \sum_l \epsilon_l a_l^\dagger a_l$$

and the number operator

$$\hat{N} = \sum_l a_l^\dagger a_l.$$

Now

$$\{a_l, a_{l'}^\dagger\} = \delta_{ll'}$$

and

$$\{a_l, a_{l'}\} = \{a_l^\dagger, a_{l'}^\dagger\} = 0.$$

The eigenvalues of the number operator related to the state l,

$$\hat{n}_l = a_l^\dagger a_l,$$

are

$$n_l = 0, 1.$$

The state sum in the grand canonical ensemble is

$$\begin{aligned} &Z_{\mathrm{G,FD}} \\ &\quad = \mathrm{Tr}\, e^{-\beta(\hat{H}-\mu\hat{N})} \\ &\quad = \sum_{n_1=0}^{1}\sum_{n_2=0}^{1} \cdots \left\langle n_1 n_2 \cdots \left| e^{-\beta(\hat{H}-\mu\hat{N})} \right| n_1 n_2 \cdots \right\rangle \\ &\quad = \sum_{n_1=0}^{1}\sum_{n_2=0}^{1} \cdots e^{-\beta \sum_l n_l(\epsilon_l-\mu)} \\ &\quad = \prod_l \left\{ \sum_{n=0}^{1} e^{-\beta n(\epsilon_l-\mu)} \right\} \\ &\quad = \prod_l \left[1+e^{-\beta(\epsilon_l-\mu)}\right]. \end{aligned}$$

The grand potential is

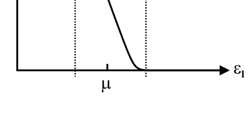
$$\Omega_{\mathrm{FD}} = -k_B T \sum_l \ln\left[1+e^{-\beta(\epsilon_l-\mu)}\right].$$

The average occupation number of the state l is

$$\begin{aligned} \bar{n}_l &= \langle n_l \rangle = \frac{1}{Z_{\mathrm{G,FD}}} \mathrm{Tr}\, \hat{n}_l e^{-\beta(\hat{H}-\mu\hat{N})} \\ &= \frac{1}{Z_{\mathrm{G,FD}}} \sum_{n_1=0}^{1}\sum_{n_2=0}^{1} \cdots n_l e^{-\beta \sum_{l'} n_{l'}(\epsilon_{l'}-\mu)} \\ &= -\frac{1}{\beta}\frac{\partial \ln Z_{\mathrm{G,FD}}}{\partial \epsilon_l} = \frac{\partial \Omega_{\mathrm{FD}}}{\partial \epsilon_l} \\ &= \frac{e^{-\beta(\epsilon_l-\mu)}}{1+e^{-\beta(\epsilon_l-\mu)}}. \end{aligned}$$

Thus the *Fermi-Dirac occupation number* can be written as

$$\bar{n}_l = \frac{1}{e^{\beta(\epsilon_l-\mu)}+1}.$$

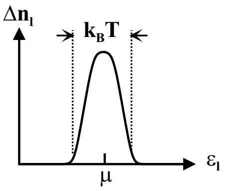


The expectation value of the square of the occupation number will be

$$\begin{aligned}
\langle n_l^2 \rangle &= \frac{1}{Z_{\mathrm{G,FD}}} \operatorname{Tr} \hat{n}_l^2 e^{-\beta(\hat{H}-\mu\hat{N})} \\
&= \frac{1}{Z_{\mathrm{G,FD}}} \sum_{n_1=0}^{1} \sum_{n_2=0}^{1} \cdots n_l^2 e^{-\beta \sum_{l'} n_{l'}(\epsilon_{l'}-\mu)} \\
&= \frac{1}{\beta^2} \frac{1}{Z_{\mathrm{G,FD}}} \frac{\partial^2 Z_{\mathrm{G,FD}}}{\partial {\epsilon_l}^2} \\
&= -\frac{1}{\beta} \frac{1}{Z_{\mathrm{G,FD}}} \left(\prod_{l' \neq l} \left[1 + e^{-\beta(\epsilon_{l'}-\mu)} \right] \right) \\
&\quad \times \frac{\partial}{\partial \epsilon_l} e^{-\beta(\epsilon_l-\mu)} \\
&= \frac{e^{-\beta(\epsilon_l-\mu)}}{1+e^{-\beta(\epsilon_l-\mu)}} = \bar{n}_l .
\end{aligned}$$

This is natural, since $n_l^2 = n_l$.
For the variance we get

$$\begin{aligned}
(\Delta n_l)^2 &= \langle n_l^2 \rangle - \langle n_l \rangle^2 = \bar{n}_l - \bar{n}_l^2 \\
&= \bar{n}_l (1-\bar{n}_l).
\end{aligned}$$



There are fluctuations only in the vicinity of the chemical potential μ.
The *entropy* is

$$\begin{aligned}
S &= -\frac{\partial \Omega}{\partial T} \\
&= k_B \sum_l \ln \left[1 + e^{-\beta(\epsilon_l-\mu)} \right] \\
&\quad + \frac{1}{T} \sum_l \overbrace{\frac{e^{-\beta(\epsilon_l-\mu)}}{1+e^{-\beta(\epsilon_l-\mu)}}}^{=\bar{n}_l} (\epsilon_l - \mu).
\end{aligned}$$

Now $\beta(\epsilon_l-\mu) = \ln \frac{1-\bar{n}_l}{\bar{n}_l}$ and $1+e^{-\beta(\epsilon_l-\mu)} = \frac{1}{1-\bar{n}_l}$, so

$$S = -k_B \sum_l \left[(1-\bar{n}_l) \ln(1-\bar{n}_l) + \bar{n}_l \ln \bar{n}_l \right].$$