1 What is the chemical potential

La probabilité de trouver le système dans un microétat Ω_i donné, caractérisé par un nombre n_i de particules, est donné par

$$p\left(\Omega_i\right) = \frac{1}{Z} \exp\left(-\frac{1}{k_B T}\left(n_i E - n_i \mu\right)\right) \tag{1}$$

où la fonction de partition Z assure la normalisation de la probabilité

$$Z = \sum_{\Omega_i} \exp\left(n_i \frac{E-\mu}{k_B T}\right) = \begin{cases} 1+\exp\left(-\frac{E-\mu}{k_B T}\right) & \text{fermions} \\ \frac{1}{1-\exp\left(-\frac{E-\mu}{k_B T}\right)} & \text{bosons} \end{cases} \tag{2}$$

En notant $\exp\left(-\frac{E-\mu}{k_B T}\right) = r$, le nombre moyen de particules occupant l'état est donné par

$$\langle n \rangle = \frac{1}{Z} \sum_{\Omega_i} n_i r^{n_i} = \begin{cases} \frac{r}{1+r} & \text{fermions} \\ (1-r)\,\frac{r}{(1-r)^2} & \text{bosons} \end{cases} \tag{3}$$

$$= \frac{1}{z^{-1}\exp\left(\frac{E}{k_B T}\right)+\epsilon} \text{ with } \epsilon = \begin{cases} +1 & \text{fermions} \\ -1 & \text{bosons} \\ 0 & \text{Boltzman} \end{cases} \tag{4}$$

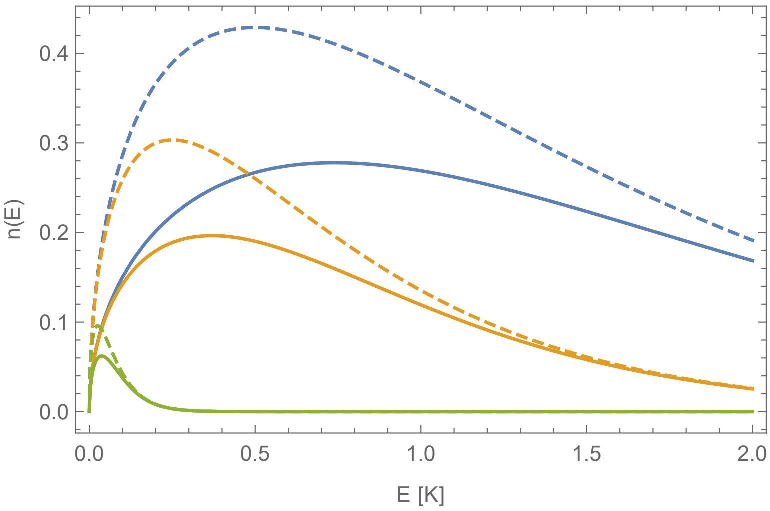
where $z = \exp \frac{\mu}{k_B T}$ is the *fugacity* of the system.

2 Grand canonical description

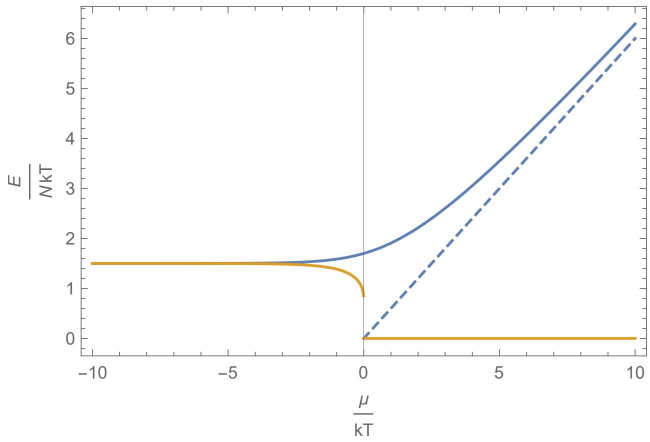
In the grand-canonical description, the chemical potential is fixed and the number of particle $N = \int dE\, \rho(E) n(E, \mu, T)$ changes with the temperature.

At fixed chemical potential, the occupation of any given energy level is smaller at lower temperature. The behavior of a quantum system is close to a Boltzmann distribution if $E - \mu \gg kT$, ie for *low temperatures*.

This is illustrated in the figure below, which shows the average occupation as a function of the energy for fermions (solid lines) and classical particles (dashed lines) at fixed μ for $T = 1\,\mathrm{K}$ (blue), $0.5\,\mathrm{K}$ (yellow) and $0.05\,\mathrm{K}$ (green). At any given energy, the discrepency between the quantum and classical distribution is small at small temperatures. The integral of the curve (ie the total number of particles) decreases with the temperature.



Below is the average energy per particule for fermions (blue) and bosons (yellow).



This graph can also be read in the canonical description (see below)

- In the classical limit $-\mu \gg k_B T$, the average energy per particule is $\frac{3}{2} k_B T$.

- For Fermions at low temperature, $\mu \to E_F$ so $\frac{\mu}{k_B T} = \frac{T_F}{T} \to +\infty$ and the average energy per particule is $\frac{3}{5} k_B T_F$.

- For Bosons at low temperature, $\mu = 0$ and the average energy for the uncondensed fraction is

$$\frac{\int dE \, \frac{E\sqrt{E}}{\exp\left(\frac{E}{k_B T}\right)-1}}{\int dE \, \frac{\sqrt{E}}{\exp\left(\frac{E}{k_B T}\right)-1}} = \frac{\Gamma_{5/2}}{\Gamma_{3/2}} \times \frac{\zeta_{5/2}}{\zeta_{3/2}} \times k_B T = 0.77 \, k_B T \tag{5}$$

3 Canonical ensemble with grand-canonical description

The situation is completely different in the canonical ensemble, where the number of particles is fixed. To keep the particle number constant regardless of the temperature, the chemical potential changes with the temperature.

For a free gas with $\rho(E) = \frac{V}{4\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \sqrt{E}$, a useful notation is to introduce the quantum temperature

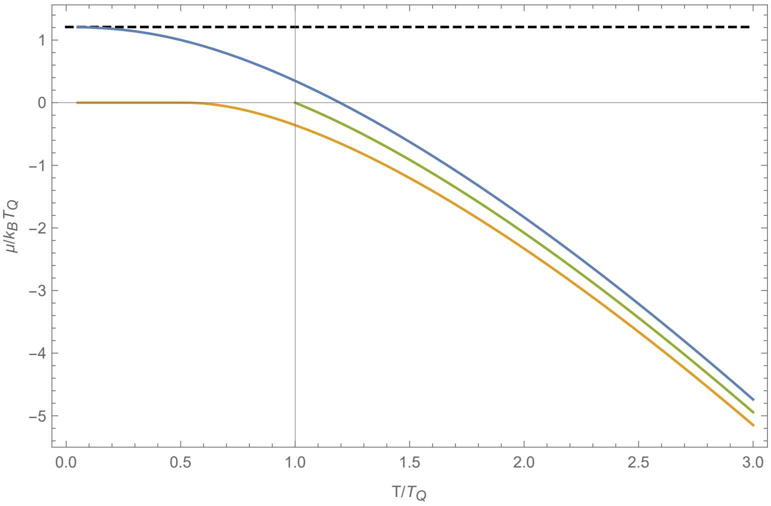
$$k_B T_Q = \frac{2\pi\hbar^2}{m} n^{2/3} \tag{6}$$

such that

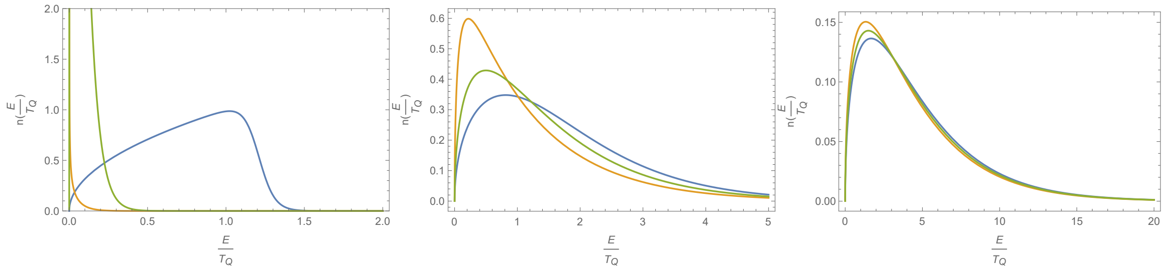
$$N = \int dE \, \frac{V}{4\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \sqrt{E} \times \frac{1}{z^{-1} \exp\left(\frac{E}{k_B T}\right) + \epsilon} \tag{7}$$

$$\Rightarrow \left(\frac{T_Q}{T}\right)^{3/2} = \frac{2}{\sqrt{\pi}} \int_0^{+\infty} du \, \frac{\sqrt{u}}{z(T)^{-1} \exp(u) + \epsilon} \tag{8}$$

and the fugacity $z(T)$ is to be adjusted so that T_Q remains constant (see figure below)



The situation is quite different for bosons, fermions and classical particles, is illustrated and explained below



Populations for fermions (blue), bosons (yellow) and classical particles (green) at $T = 0.05\,T_Q$ (left), $T = T_Q$ (center) and $T = 3\,T_Q$ (right). Here, the area (and hence number of particles) is constant regardless of the temperature - up to the Bose Einstein condensation.

Bosons

Since the denominator $\exp\left(\frac{E-\mu}{k_B T}\right) - 1$ can never become negative, the chemical potential must always be smaller than the lowest energy level of the system. For free particles, $E_{min} = 0$, and the chemical potential is always negative.

This implies that the integral in (8) saturates at 1 for $z = 1$, obtained for the critical temperature

$$\frac{T_C}{T_Q} = \left(\frac{2}{\sqrt{\pi}} \int_0^{+\infty} du \, \frac{\sqrt{u}}{\exp(u) - 1} \right)^{-2/3} = (\zeta_{3/2})^{-2/3} = 0.5272 \tag{9}$$

If the temperature is lowered below this value, the chemical potential remains stucked at 0 and the total number of particles can not be constant anymore, as if particles where disappearing from the system. The missing particles are actually accumulated in the ground state and form a Bose Einstein condensate. The fraction of condensed particles is given by

$$\frac{N_{\text{BEC}}}{N_{\text{tot}}} = 1 - \left(\frac{T}{T_C} \right)^{3/2} \tag{10}$$

Fermions

There is no phase transition for fermions. The chemical potential converges towards a finite value at 0 temperature ; all energy levels below this value are occupied and all energy levels above this value are free. The limit is defined as the Fermi energy

$$\mu(0) = k_B T_F = E_F = \frac{\hbar^2}{2m} \left(6\pi^2 n\right)^{2/3} = \frac{\left(6\pi^2\right)^{2/3}}{4\pi} \times T_Q \tag{11}$$

and is estimated as

$$4\pi^2 n \left(\frac{\hbar^2}{2m}\right)^{3/2} = \int_0^{E_F} dE\,\sqrt{E} = \frac{2}{3}E_F^{3/2} \tag{12}$$

The chemical potential crosses 0 at $T = T_F$.

Classical limit

For temperature much higher tham the quantum temperature $T \gg T_Q$, both fermions and bosons behave like classical particles and the chemical potential is well approximated by

$$\mu \sim -\frac{3}{2}k_B T \times \log\frac{T}{T_Q} \tag{13}$$

$$n = \left(\frac{2\pi\hbar^2}{mk_B T}\right)^{3/2} e^{\beta\mu} \tag{14}$$

This result is not contradictory with the previous section. This can be seen considering the complete hierarchy

$$-\mu \gg T \gg T_Q \tag{15}$$

In the previous section, μ was fixed so T had to be brought to low temperatures to reach the classical regime. At fixed μ and low T, the density is small and hence T_Q is small.

In this section, T_Q is fixed so T has to be brought to high temperatures to reach the classical regime. At fixed density and high temperature, the chemical potential is large and negative.

This is illustrated in the figure below, which pictures fermionic populations with fixed chemical potential (dashed line) and fixed density (solid line) for $T = 0.05\,T_Q$ (green), $T = 0.5\,T_Q$ (yellow) and $T = T_Q$ (blue).