4. The Bose-Einstein (DE) and Fermi-Dirac (FD) Distribution

M 11.1-4, B&S 9.7, 9.9, 10.1-3, K&K 5-6.
Quantum effects become important if the typical distance d between atoms is $d \le \lambda_T$.
Remember than λ_T depends on temperature, so that at low temperatures quantum effects also become important. Approach the problem via distribution functions.

4.1 Average Number of Particles $f(\varepsilon)$

Define $f(\varepsilon)$ as the average number of particles in a single particle state of energy ε and temperature T.

For Bosons, $f(\varepsilon) = \dfrac{1}{e^{\frac{(\varepsilon-\mu)}{k_B T}} - 1}$. This is the Bose-Einstein Distribution Function.

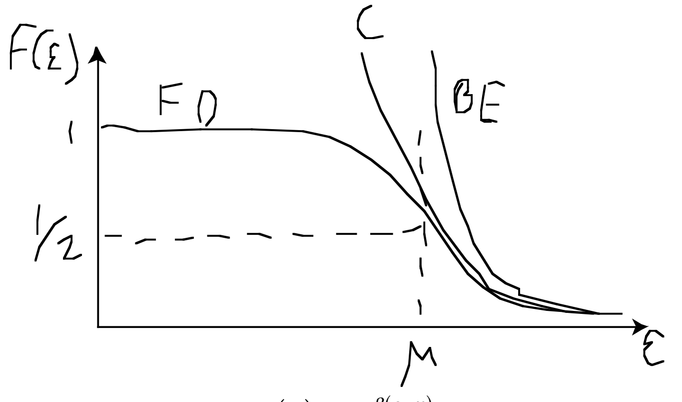
For Fermions, $f(\varepsilon) = \dfrac{1}{e^{\frac{(\varepsilon-\mu)}{k_B T}} + 1}$. This is the Fermi-Dirac Distrubition Function.

In both cases, μ is the chemical potential.

What determines the chemical potential?
The system has a fixed number of particles N.

$$N = \sum_{all\ states} f(\varepsilon) = \sum_{all\ states} \frac{1}{e^{\beta(\varepsilon-\mu)} \pm 1}$$

The energies ε of the states are known, and the temperature is known, so μ can be calculated in terms of N – or usually N/V.



For $\varepsilon - \mu >> k_B T$, $f(\varepsilon) = e^{-\beta(\varepsilon-\mu)}$ for FD and BE. They go towards the classical line (C).
The remainder of the course is devoted to the implications of $f(\varepsilon)$.

4.2 The Derivation of Fermi-Dirac Distribution Function

Consider spin ½ particles for simplicity. Consider a single-particle state of energy ε, for either spin up or spin down. Take the reservoir to be all the other single particle states, i.e. the gas as a whole.
Subtle point: states are distinguishable, particles are not.

N_s	E_s	$\mu N_s - E_s$	$p(N_s, E_s)$
0	0	0	$1/\zeta_G$

1	ε	$\mu-\varepsilon$	$\dfrac{e^{\beta(\mu-\varepsilon)}}{\zeta_G}$

$\zeta_G = 1 + e^{\beta(\mu-\varepsilon)}$

NB: lower case ζ now refers to a single state, not a single particle.

(Grand canonical partition $Z_G = \sum_{(N_s,S)} e^{\beta(\mu N_s - E_s)}$)

We are considering one state and $N_s = 0,1$.

We are after the average number of particles in the state:

$$f(\varepsilon) = \sum_{N_s,E_s} N_s p(N_s, E_s)$$

$$= 0 \times \frac{1}{\zeta_G} + 1 \times \frac{e^{\beta(\mu-\varepsilon)}}{\zeta_G}$$

$$= \frac{e^{\beta(\mu-\varepsilon)}}{1+e^{\beta(\mu-\varepsilon)}}$$

Therefore $f(\varepsilon) = \dfrac{1}{e^{\beta(\varepsilon-\mu)}+1}$.

4.3 Derivation of the Bose-Einstein Distribution Function

N_s	E_s	$\mu N_s - E_s$	
0	0	0	
1	ε	$\mu-\varepsilon$	
2	2ε	$2(\mu-\varepsilon)$	
…	…	…	
N_s	$N_s\varepsilon$	$N_s(\mu-\varepsilon)$	
…	…	…	

$\zeta_G = 1 + e^{\beta(\mu-\varepsilon)} + e^{2\beta(\mu-\varepsilon)} + \ldots + e^{N_s\beta(\mu-\varepsilon)} + \ldots$

$$= \sum_{N_s=0}^{\infty} e^{N_s x}$$

where $x = \beta(\mu-\varepsilon)$

This is just a geometric series with ratio $r = e^x$.

$$1 + r + r^2 + \ldots = \frac{1}{1-r}$$

So $\zeta_G = \dfrac{1}{1-e^x}$.

$$f(\varepsilon) = \frac{\sum_{N_s=0}^{\infty} N_s e^{N_s x}}{\zeta_G} = \frac{\frac{\partial \zeta_G}{\partial x}}{\zeta_G} = \frac{\partial \ln \zeta_G}{\partial x} = -\frac{\partial \ln(1-e^x)}{\partial x} = \frac{e^x}{1-e^x} = \frac{1}{e^{-x}-1}$$

$$= \frac{1}{e^{\frac{\varepsilon-\mu}{k_B T}} - 1}$$

4.4 Calculation of the Grand Partition Function, Pressure etc.

$$Z_G = \prod_{all\ single\ particle\ states} \zeta_G$$

where Z_G is for the whole system.

cf. $Z = \zeta^N$ for distinguishable particles in a classical gas.

$$\phi = -k_B T \ln Z_G = -k_B T \sum_{all\ single\ particle\ states} \ln \zeta_G$$

i.e. each single particle state contributes additively to $\phi(= -pV)$).

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

(constant V means ε does not change.)

$S = -k_B \sum_{states} \left[f(\varepsilon) \ln f(\varepsilon) + (1 - f(\varepsilon)) \ln (1 - f(\varepsilon)) \right]$ for Fermions

$S = -k_B \sum_{states} \left[f(\varepsilon) \ln f(\varepsilon) - (1 + f(\varepsilon)) \ln (1 + f(\varepsilon)) \right]$ for Bosons.

(This is not examinable as it needs a lot of algebra…)

(b) $p = -\left(\frac{\partial \phi}{\partial V}\right)_{T,\mu}$

For particles in a box,

$$\frac{\partial \phi}{\partial V} = \frac{\partial \phi}{\partial \varepsilon} \frac{\partial \varepsilon}{\partial V}$$

$\varepsilon = \frac{\hbar^2 k^2}{2M}$, $k^2 \sim \frac{1}{L^2}$, $V = L^3$.

$$\frac{\partial \varepsilon}{\partial V} = \frac{\partial \varepsilon}{\partial L} \frac{\partial L}{\partial V} = -2 \frac{\varepsilon}{L} \frac{1}{3L^2} = \frac{2}{3} \frac{\varepsilon}{V}$$

$$\sum_{states} \frac{\partial \phi}{\partial \varepsilon} = \sum_{states} \frac{\partial \left(-k_B T \ln \left(1 + e^{\beta(\mu - \varepsilon)} \right) \right)}{\partial \varepsilon}$$

$$= \frac{2}{3V} \underbrace{\sum_{states} \varepsilon f(\varepsilon)}_{E}$$

This is true for both FD and BE distribution.

$p = \frac{2E}{3V}$. Therefore $pV = \frac{2}{3} E$.

Classically, $E = \frac{3}{2} NkT$. So $pV = Nk_B T$.