EE201/MSE207 Lecture 14

Particle distributions at $T \neq 0$ (quantum statistics)

Classical statistical mechanics

1. Microcanonical ensemble

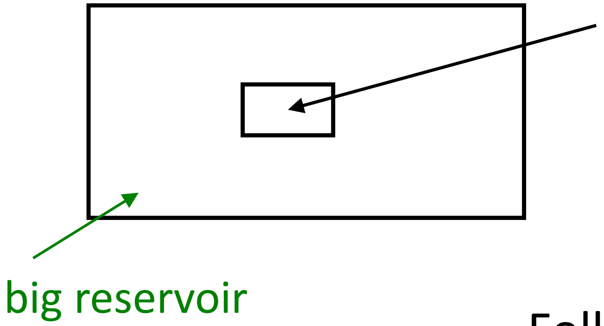
$N = \text{const}$

$E = \text{const}$

(gas of particles distributed among energy/velocity levels)

All microstates are equally probable (postulate)

2. Canonical ensemble



$N = \text{const}$

$E \neq \text{const}$ (exchange of heat)

Probability of a state $P(E) \propto e^{-E/T}$

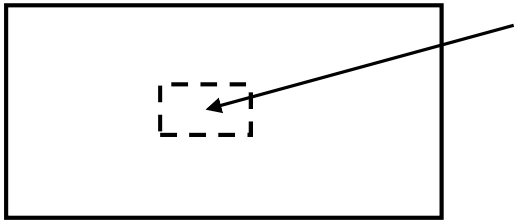
$(k_B = 1,\ k_B T \to T)$

Follows from the postulate for microcaconical ensemble

(this is how temperature is introduced)

Classical statistical mechanics (cont.)

3. Grand canonical ensemble



$N \neq \text{const}$ (particles can penetrate)

$E \neq \text{const}$

Probability of a state $P(E,N) \propto e^{-(E-\mu N)/T}$

(two parameters: temperature and chemical potential)

Chemical potential μ: average energy cost of bringing an extra particle from big reservoir

The formula for $P(E,N)$ also follows from equiprobability in microcanonical ens.

From $P(E,N)$ we can derive $n(\varepsilon)$: average number of particles with energy ε

$E = \sum_i n(\varepsilon_i)\, \varepsilon_i$

$$\boxed{n(\varepsilon) = \exp\left(-\frac{\varepsilon-\mu}{T}\right)}$$

Maxwell-Boltzmann distribution

Derivation P_k: probability to have k particles with quantized (binned) energy ε

$P_k = P_0\, e^{-k(\varepsilon-\mu)/T}/k!$ ($k!$ comes from number of combinations)

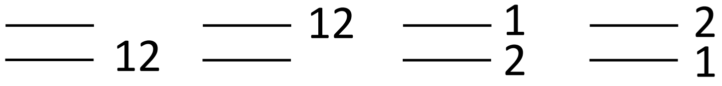
$$\sum_{k=0}^{\infty} P_k = 1 \quad \Rightarrow \quad P_0 = 1/\exp[\exp(-(\varepsilon-\mu)/T)] \quad \Rightarrow \quad \bar{k} = \exp[-(\varepsilon-\mu)/T]$$

Quantum statistics

Main difference: indistinguishable particles (instead of a question "which one" we are only allowed to ask "how many")

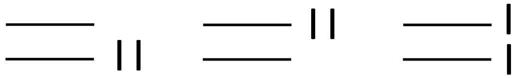
Example: two particles on two levels

classical



equal probabilities, 1/4 each

quantum



equal probabilities, 1/3 each

Fermions

Either 0 or 1 particle on a level with energy ε (spin increases number of levels, still no 2 particles on the same level)

$$\begin{cases} \dfrac{P_1}{P_0} = e^{-(\varepsilon-\mu)/T} \\ P_0 + P_1 = 1 \end{cases}$$

Still use classical relation $P(E,N) \propto e^{-(E-\mu N)/T}$

$$\Rightarrow \qquad P_0 = \frac{1}{1+e^{-(\varepsilon-\mu)/T}}, \quad P_1 = \frac{e^{-(\varepsilon-\mu)/T}}{1+e^{-(\varepsilon-\mu)/T}},$$

$$\Rightarrow \quad \boxed{\bar{n} = P_1 = \frac{1}{1+e^{(\varepsilon-\mu)/T}}}$$

Fermi-Dirac distribution (Fermi statistics)

μ is Fermi level (chemical vs. electrochemical)

Quantum statistics (cont.)

Bosons

$$\frac{P_1}{P_0} = e^{-(\varepsilon-\mu)/T}, \quad \frac{P_2}{P_0} = e^{-2(\varepsilon-\mu)/T}, \quad \frac{P_3}{P_0} = e^{-3(\varepsilon-\mu)/T}, \quad \ldots$$

$$\sum P_n = 1 \quad \Rightarrow \quad P_0 = \frac{1}{1 + e^{-(\varepsilon-\mu)/T} + e^{-2(\varepsilon-\mu)/T} + \ldots} = 1 - e^{-(\varepsilon-\mu)/T}$$

$$\bar{n} = 0 \cdot P_0 + 1 \cdot P_1 + 2 \cdot P_2 + \ldots = \left(1 - e^{-\frac{\varepsilon-\mu}{T}}\right)\left(1 \cdot e^{-\frac{\varepsilon-\mu}{T}} + 2 \cdot e^{-2\frac{\varepsilon-\mu}{T}} + \cdots\right)$$

$$= \left(1 - e^{-\frac{\varepsilon-\mu}{T}}\right)\left(\frac{e^{-\frac{\varepsilon-\mu}{T}}}{1 - e^{-\frac{\varepsilon-\mu}{T}}} + \frac{e^{-2\frac{\varepsilon-\mu}{T}}}{1 - e^{-\frac{\varepsilon-\mu}{T}}} + \cdots\right) = \frac{e^{-\frac{\varepsilon-\mu}{T}}}{1 - e^{-\frac{\varepsilon-\mu}{T}}}$$

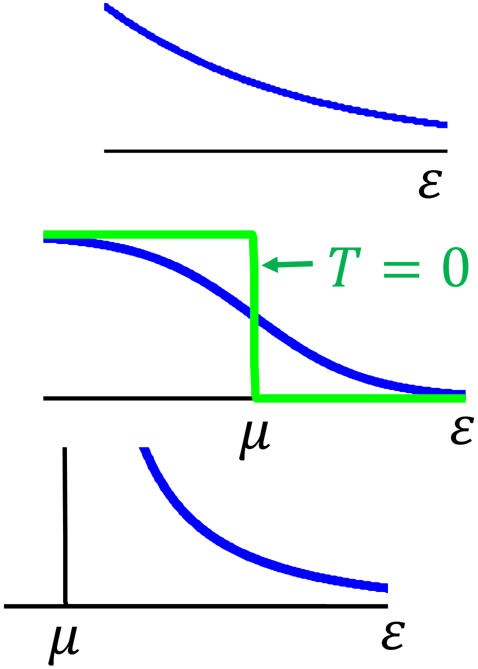
$$\boxed{\bar{n} = \frac{1}{e^{(\varepsilon-\mu)/T} - 1}}$$

Bose-Einstein distribution
(Bose statistics)

$\mu \le 0$ (if energy starts from 0),
otherwise infinity at $\varepsilon = \mu$

Particle distributions: summary

$$n(\varepsilon) = \begin{cases} e^{-(\varepsilon-\mu)/T} & \text{Maxwell-Boltzmann (Boltzmann)} \\[2ex] \dfrac{1}{e^{(\varepsilon-\mu)/T}+1} & \text{Fermi-Dirac (Fermi)} \\[2ex] \dfrac{1}{e^{(\varepsilon-\mu)/T}-1} & \text{Bose-Einstein (Bose)} \end{cases}$$



μ is Fermi level

To find μ: $N = \int n(\varepsilon)\, D(\varepsilon)\, d\varepsilon$

density of states

$n(\varepsilon)$ depends on temperature
$\Rightarrow$ μ depends on temperature

Remark 1. Often notation $f(\varepsilon)$ instead of $n(\varepsilon)$, especially for Fermi distribution

Remark 2. Large-ε tails of Fermi-Dirac and Bose-Einstein distributions coincide with Maxwell-Boltzmann distribution

2D case

(not in textbook)

$$\frac{D(\varepsilon)}{A} = \frac{m}{2\pi\hbar^2}\,(2s+1)$$

$D(\varepsilon)$ is density of states, A is area

s is spin, in general $2s+1$ is degeneracy

Electrons (Fermi, $s = 1/2$)

$$\frac{N}{A} = \int_0^\infty \frac{m}{2\pi\hbar^2}\,\overset{\text{spin}}{2}\,\frac{1}{e^{(\varepsilon-\mu)/T}+1}\,d\varepsilon = \frac{m}{2\pi\hbar^2}\,\overset{\text{spin}}{2}\,T\ln(1+e^{\mu/T})$$

No spin factor of 2 in high magnetic field

Bosons with $s = 0$

$$\frac{N}{A} = \int_0^\infty \frac{m}{2\pi\hbar^2}\,\frac{1}{e^{(\varepsilon-\mu)/T}-1}\,d\varepsilon = \frac{m}{2\pi\hbar^2}\,T\ln(1-e^{\mu/T})$$

3D case

$$\frac{D(\varepsilon)}{V} = \frac{m^{3/2}\varepsilon^{1/2}}{\sqrt{2}\,\pi^2\hbar^3}\,(2s+1)$$

$D(\varepsilon)$ is density of states, V is volume

s is spin, in general $2s+1$ is degeneracy
(including valleys, etc.)

$$\frac{N}{V} = \int_0^\infty \frac{m^{3/2}\varepsilon^{1/2}}{\sqrt{2}\,\pi^2\hbar^3}\,\frac{1}{e^{(\varepsilon-\mu)/T}\pm 1}\,(2s+1)\,d\varepsilon$$

degeneracy

$$\frac{E}{V} = \int_0^\infty \varepsilon\,\frac{m^{3/2}\varepsilon^{1/2}}{\sqrt{2}\,\pi^2\hbar^3}\,\frac{1}{e^{(\varepsilon-\mu)/T}\pm 1}\,(2s+1)\,d\varepsilon$$

(e.g., for heat capacity)

Fermi: “+”, Bose: “−”

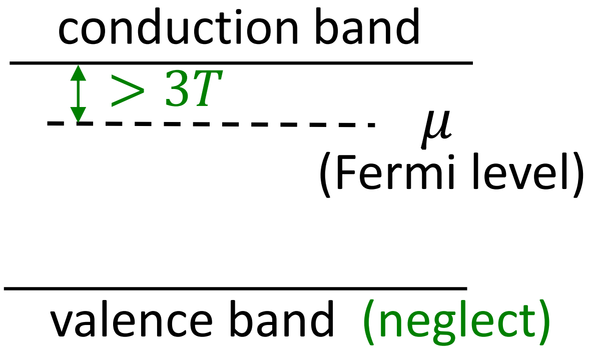
Unfortunately, these integrals cannot be calculated analytically.

Simplification if $-\mu \gg T$, then F-D and B-E distributions reduce to M-B.

$$\frac{1}{e^{(\varepsilon-\mu)/T}\pm 1} \approx e^{-(\varepsilon-\mu)/T} \qquad \text{when} \qquad \varepsilon-\mu \gg T$$

Nondegenerate semiconductor

Assume n-type (p-type similar), $-\mu \gg T$, $2s+1=2$



$$\frac{N}{V} \approx \int_0^\infty \frac{m^{3/2}\varepsilon^{1/2}}{\sqrt{2}\,\pi^2\hbar^3} e^{-(\varepsilon-\mu)/T} 2\, d\varepsilon = \ldots$$

$$= 2\, e^{\mu/T} \left(\frac{mT}{2\pi\hbar^2}\right)^{3/2}$$

Room temperature: $T = 26$ meV

$$\boxed{\mu = T \ln\left[\frac{N}{V}\,\frac{1}{2}\left(\frac{2\pi\hbar^2}{mT}\right)^{3/2}\right]}$$

degeneracy; can be larger, Si: 2×6

$$\frac{E}{V} \approx \int_0^\infty \varepsilon\, \frac{m^{3/2}\varepsilon^{1/2}}{\sqrt{2}\,\pi^2\hbar^3} e^{-(\varepsilon-\mu)/T} 2\, d\varepsilon = \ldots = \frac{3}{2} T\, \frac{N}{V}$$

$$\boxed{E = \frac{3}{2} T N}$$

Bose-Einstein condensation

For Bose-Einstein distribution usually $\mu < 0$ (cannot be $\mu > 0$).

However, at small enough T, it becomes $\mu = 0$, then

$$\frac{N}{V} = \int_0^\infty \frac{m^{3/2}\varepsilon^{1/2}}{\sqrt{2}\,\pi^2\hbar^3}\,\frac{1}{e^{-\mu/T} - 1}\,d\varepsilon = 2.61\left(\frac{mT}{2\pi\hbar^2}\right)^3 \qquad (s = 0)$$

Therefore critical temperature $$T_c = \frac{2\pi\hbar^2}{m}\left(\frac{N}{2.61\,V}\right)^{2/3}$$

Below T_c particles crowd into the ground state
(finite fraction of all particles occupy ground state)

Different calculation: $$N = N(0) + \int n(\varepsilon)\,D(\varepsilon)\,d\varepsilon$$

Examples: superconductivity, superfluidity, B-E condensation of atoms

Massless particles (photons, phonons)

$$\varepsilon = \hbar\omega \qquad k = \frac{2\pi}{\lambda} = \frac{\omega}{c}$$

speed of light or sound velocity

Number of particles is not conserved $\Rightarrow$ $\boxed{\mu = 0}$ (creation of extra particle does not cost extra energy)

$$n(\omega) = \frac{1}{e^{\hbar\omega/T} - 1}$$ (bosons)

DOS: $$dN = \frac{dx\,dk_x\ \ dy\,dk_y\ \ dz\,dk_z}{(2\pi)^3} \quad \Rightarrow \quad \frac{dN}{V} = \frac{dk_x\,dk_y\,dk_z}{(2\pi)^3}$$

$$\frac{dN}{V\,d\omega} = \frac{4\pi k^2}{(2\pi)^3}\,\frac{dk}{d\omega} = \frac{\omega^2}{2\pi^2 c^3}$$

× 2 for photons (two polarizations)

× 3 for phonons, better $\frac{2}{c_\perp^3} + \frac{1}{c_\parallel^3}$

Average energy per dω (for photons)

$$\frac{dE}{V\,d\omega} = \hbar\omega\,\frac{2\omega^2}{2\pi^2 c^3}\,\frac{1}{e^{\hbar\omega/T} - 1} = \frac{2\hbar\omega^3}{2\pi^2 c^3 (e^{\hbar\omega/T} - 1)}$$

(Planck's formula)