Foundations of Physics 2B/3C 2019-2020

Thermodynamics – Lecture 13 Recap

- Reviewed Thermodynamics.
- Were introduced to the topic of Statistical Mechanics.
- Consider distinguishable particles and how to count them,

$$\Omega = \frac{N!}{\prod_j n_j!},$$

for a system having N particles, with n_j in a state of energy ε_j.
- Defined entropy and temperature statistically,

$$S = k_B \ln \Omega, \quad \beta = \frac{1}{k_B T}.$$

- Saw how Boltzmann distribution, for thermal equilibrium arises.

Thermodynamics – Lecture 14 Aims

- To consider the conditions that result in the Boltzmann distribution.
- To see how the Partition function normalises the Boltzmann distribution and how it is related to classical thermodynamics.
- To look at distribution function for indistinguishable particles.
- To consider Fermion and Bosons, and in particular look at the effect of Bose-Einstein condensation, and the Fermi energy.

Boltzmann – canonical ensemble at thermal equilibrium

$$P(\varepsilon_j) \propto \exp(-\varepsilon_j / k_B T) = \exp(-\beta \varepsilon_j)$$

Ensemble – make copies of system to do statistics.

Prof 23.1 Any system has

- Fixed particle number $N = \sum n_j$, $dN = \sum_j dn_j = 0$
- Fixed total energy $E = \sum_j \varepsilon_j n_j$, $dE = \sum_j \varepsilon_j dn_j = 0$
- Most probable macrostate at thermal equilibrium $d\Omega = 0$

$$\Rightarrow \sum_j \ln(n_j)\, dn_j = 0$$

Three conditions are zero together. Lagrange Multipliers

quantities are zero can add arbitrary multiples of each and the sum is still zero

$$0 = \sum_j (\alpha\, dn_j + \beta \varepsilon_j dn_j + \ln \ln_j)\, dn_j)$$

Holds for all j: $= \sum_j dn_j (\alpha + \beta \varepsilon_j + \ln \ln_j)) = 0$

$$\alpha + \beta \varepsilon_j + \ln \ln_j) = 0$$

$$\ln \ln_j) = -\alpha - \beta \varepsilon_j$$

$$n_j = \exp(-\alpha - \beta \varepsilon_j) = \underline{A \exp(-\beta \varepsilon_j)}$$

$A = \exp(-\alpha)$ is our normalisation

Require $\sum_j P(\varepsilon_j) = 1$ [Sum of probabilities $= 1$]

$$P(\varepsilon_j) = \frac{n_j}{N} \implies 1 = \frac{1}{N} \sum n_j$$

$$1 = \frac{1}{N} \sum_j A \exp(-\beta \varepsilon_j)$$

$$A = \frac{N}{\sum_j \exp(-\beta \varepsilon_j)}, \quad Z = \sum_j \exp(-\beta \varepsilon_j)$$

Partition function

See DUO notes that $\beta = \frac{1}{k_B T}$ (defines temperature)

24. Partition function

Normalise the probability for particles (distinguishable)

$$\boxed{Z = \sum_j \exp(-\beta \varepsilon_j) = \sum_j \exp(-\varepsilon_j/k_B T)}$$

Tells us our N particles are split into i states with state j of energy ε_j, and the splitting happens in the ratio of the Boltzmann factors

Can relate Z to classical thermodynamics is via the Helmholtz

$$F = -k_B T \ln Z \implies Z = \exp(-\beta F)$$

If can write partition function for any system (know the state energies) can calculate classical thermodynamic quantities

$$F = U - TS \qquad dF = -SdT - pdV \qquad p = -\left(\frac{\partial F}{\partial V}\right)_T$$

$$U = \langle E \rangle = -\frac{d\ln(Z)}{d\beta} = k_B T^2 \frac{d\ln Z}{dT}$$

Internal energy E
in stat mechanics

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Thermodynamics – Handout 14

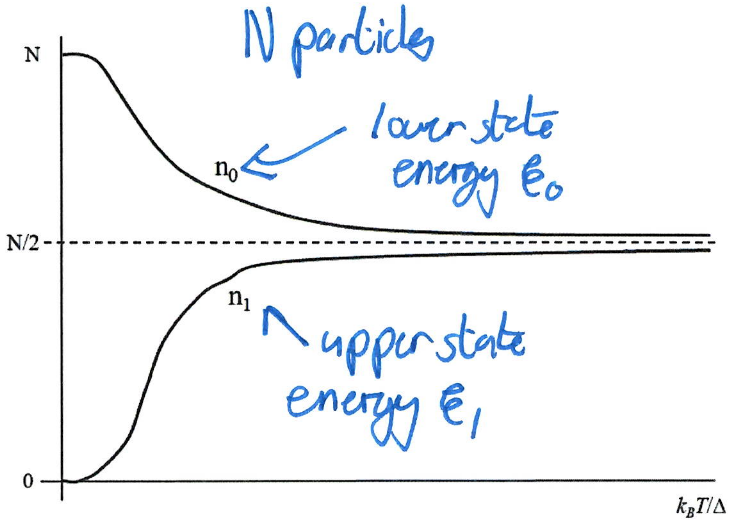


Figure 36: Populations of a system having two energy levels, and how they vary with temperature.

$\Delta = \varepsilon_1 - \varepsilon_0$

$N = n_0 + n_1$

$$P(\varepsilon_0) = \frac{n_0}{N}$$

$$= \frac{\left(A\exp\left(\frac{-\varepsilon_0}{k_BT}\right)\right)}{A\exp\left(\frac{-\varepsilon_0}{k_BT}\right) + A\exp\left(\frac{-\varepsilon_1}{k_BT}\right)}$$

$$= \frac{1}{1+\exp\left(\frac{-\Delta}{k_BT}\right)}$$

$$P(\varepsilon_1) = \frac{n_1}{N} = \frac{\exp\left(\frac{-\Delta}{k_BT}\right)}{1+\exp\left(\frac{-\Delta}{k_BT}\right)}.$$

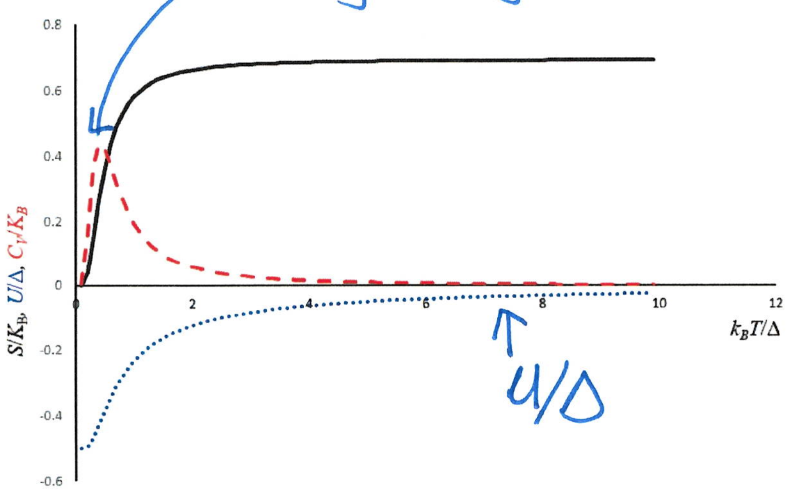
$$As\ T \to 0, P(\varepsilon_0) = \frac{1}{1+e^{-\infty}} = 1 \quad ; \quad P(\varepsilon_1) = \frac{e^{-\infty}}{1+e^{-\infty}} = 0$$

All at low energy state

$$As\ T \to \infty, P(\varepsilon_0) = \frac{1}{1+e^{-0}} = 1/2 \quad ; \quad P(\varepsilon_1) = \frac{e^{-0}}{1+e^{-0}} = \frac{1}{2}.$$

Equal state occupation

Schottky anomaly $T \sim \Delta / k_B$



The internal energy (solid, entropy (dotted) and heat capacity (dashed) for a two-state system.

$Z = \sum_j \exp(-\varepsilon_j / k_BT)$

$$Z = \exp\left(-\frac{\varepsilon_0}{k_BT}\right) + \exp\left(-\frac{\varepsilon_1}{k_BT}\right)$$

$$= 2\cosh\left(\frac{\Delta}{2k_bT}\right)$$

$$E(=U) = -\frac{d\ln Z}{d\beta} = -\frac{1}{Z} \times \frac{dZ}{d\beta}$$

$$= -\frac{1}{2\cosh(\beta\Delta/2)} \times 2 \times \frac{\Delta}{2}\sinh(\beta\Delta/2)$$

$$= -\frac{\Delta}{2}\tanh(\beta\Delta/2).$$

$F = U - TS$

$\uparrow$

E

$F = -k_BT\ln Z$

$$S = S = \frac{E-F}{T} = -\frac{\Delta}{2T}\tanh\left(\frac{\beta\Delta}{2}\right) + k_BT\ln\left(2\cosh\left(\frac{\beta\Delta}{2}\right)\right).$$

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V = k_B\left(\frac{\Delta\beta}{2}\right)^2 \operatorname{sech}^2\left(\frac{\beta\Delta}{2}\right).$$

$C_V = \left(\frac{\partial Q}{\partial T}\right)_V$

As $T \to 0$, $E \to -\Delta/2$ and $S \to 0$ [System all in lower level]

$S = k_B \ln \Omega$ with $\Omega = 1$

As $T \to \infty$, $E \to 0$ (equal state occupation) $S = k_B \ln 2$

25 Indistinguishable Particles

Cannot label them
- Classical (dilute) gas, particles are spread out in the system
- Fermions + Bosons, are identical types of quantum particle with differing wavefunctions

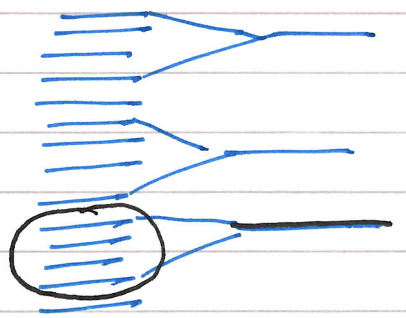
Quantum effects can change the statistics

$$\psi(1,2) = \frac{1}{\sqrt{2}}\left[\psi_A(1)\psi_B(2) \pm \psi_A(2)\psi_B(1)\right]$$

Bosons have a symmetric wavefunction, and allows any number of particles to occupy a given quantum state. Integer spin.

Fermions have antisymmetric wavefunction. Satisfy the Pauli exclusion principle, no two particles occupy the same quantum state. Half integer spin.

Density of states
- Gases have many allowed ~~levels~~ states than particles, group our energy states into levels



ith level energy ε_i, has g_i quantum states

True Grouped

Density of states g_i — how many energy states can exist

$f_i = \frac{n_i}{g_i}$ distribution function, Number of particles in a given state

Many energies, we can take energy to be continuous, and consider how many particles in the energy $\varepsilon \rightarrow \varepsilon + d\varepsilon$

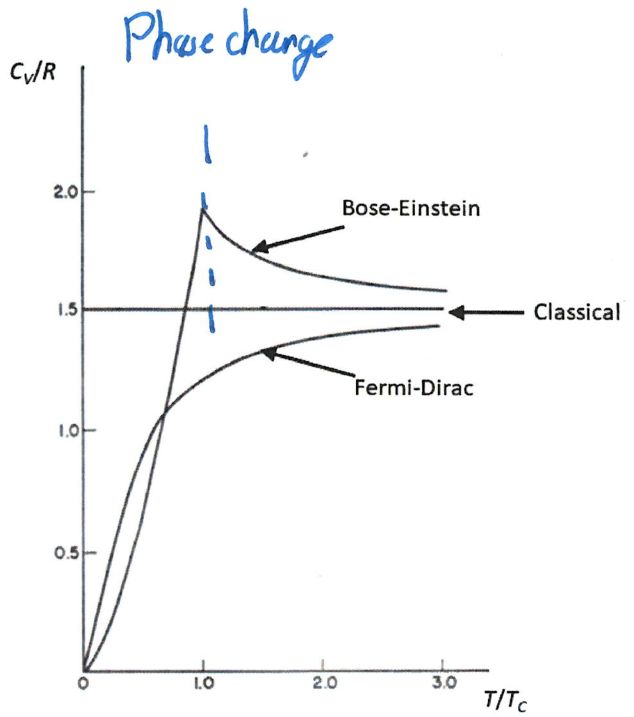
$$n(\varepsilon)d\varepsilon = f(\varepsilon)g(\varepsilon)d\varepsilon$$

$$N = \int_0^\infty n(\varepsilon)d\varepsilon \quad , \quad E = \int \varepsilon n(\varepsilon)d\varepsilon$$

Maxwell Boltzmann $\quad f(\varepsilon) = A \exp\left(\frac{-\varepsilon}{k_B T}\right)$

Bose-Einstein $\quad f_{BE}(\varepsilon) = \frac{1}{\exp\left(\frac{\varepsilon - \mu}{k_B T}\right) - 1}$

Fermi Dirac $\quad f_{FD}(\varepsilon) = \frac{1}{\exp\left(\frac{\varepsilon - \varepsilon_F}{k_B T}\right) + 1}$



Heat capacity behaviour with temperature for various particles.

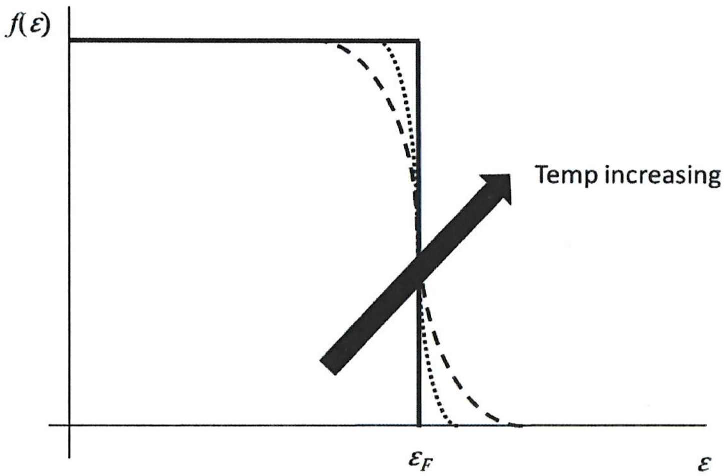


Figure 38: The behaviour of the Fermi-Dirac distribution with temperature.

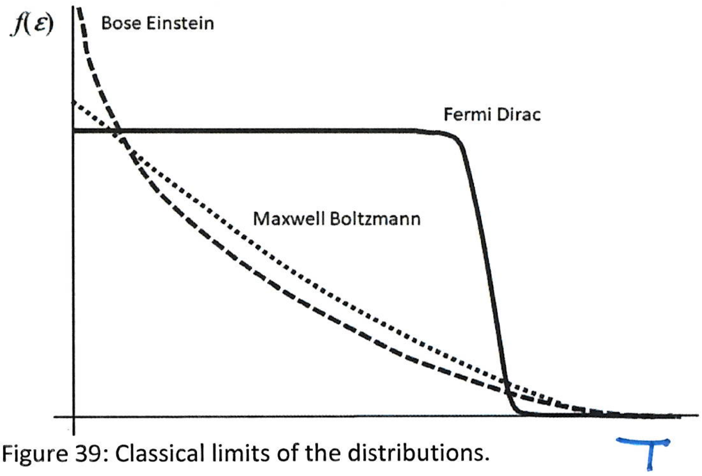


Figure 39: Classical limits of the distributions.

Bose Einstein

μ is the chemical potential

As $T \to 0$, $\mu \to \varepsilon_0$

$$\lim_{T \to 0} \exp\left(\frac{\varepsilon - \mu}{k_B T}\right) = 1$$

$$f_{BE}(\varepsilon) \to \frac{1}{1-1} = \frac{1}{0} \to \infty$$

All Bosons go to the lowest quantum state.
– Bose-Einstein condensation

ε_F – Fermi energy

At $T = 0$ $\varepsilon \to \varepsilon_F$

$$f_{FD}(\varepsilon) = \frac{1}{1+1} = \frac{1}{2}$$

As $T \to \infty$ $f_{FD} \to 0$

At $T=0$ all states filled to Fermi energy

At high T all distributions become the same.