

PART IX

- 1) Boltzmann distribution
- 2) Examples
- 3) Thermodynamic potentials
- 4) Maximum work
- 5) Equilibrium conditions
- 6) Examples

Consider a quantum system in a heat bath with temperature T .

The energy of the system can take values $\epsilon_i = \epsilon_0, \epsilon_1, \epsilon_2 \dots$ that correspond to the quantum states $|i\rangle$.

The probability to find the system in the quantum state $|i\rangle$ is given by

$$w_i = \frac{1}{Z} e^{-\frac{\epsilon_i}{kT}}$$

$\frac{1}{Z}$ is the normalization constant.

The distribution is called:

Boltzmann distribution \approx Gibbs distribution \approx Canonical distribution

Classical Boltzmann distribution

$$w(x) = \frac{1}{Z} e^{-\frac{U(x)}{kT}} dx$$

and Maxwell velocity distribution

$$w(\vec{v}) = \frac{1}{Z} e^{-\frac{mv^2}{kT}} d^3v$$

are just special cases of the general Boltzmann distribution

The Boltzmann distribution can be derived (3rd year statistical physics) from the microcanonical distribution

Normalization condition

$$\sum_i w_i = 1 = \frac{1}{Z} \sum_i e^{-\frac{\epsilon_i}{kT}} \Rightarrow$$

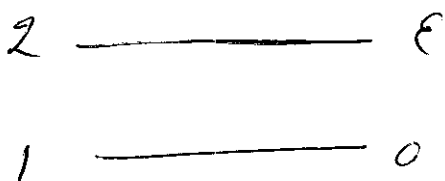
$$\Rightarrow Z = \sum_i e^{-\frac{\epsilon_i}{kT}}$$

Average energy of the system

$$\bar{E} = \sum_i \epsilon_i w_i = \frac{1}{Z} \sum_i \epsilon_i e^{-\frac{\epsilon_i}{kT}}$$

Examples:

(I) 2 level system without degeneracy.

$$\left\{ \begin{array}{l} w_1 = \frac{1}{Z} e^{-\frac{0}{kT}} = \frac{1}{Z} = \frac{1}{1 + e^{-\epsilon/kT}} \\ w_2 = \frac{1}{Z} e^{-\frac{\epsilon}{kT}} = \frac{e^{-\epsilon/kT}}{1 + e^{-\epsilon/kT}} \end{array} \right.$$


$$Z = \sum_i e^{-\frac{\epsilon_i}{kT}} = 1 + e^{-\frac{\epsilon}{kT}}$$

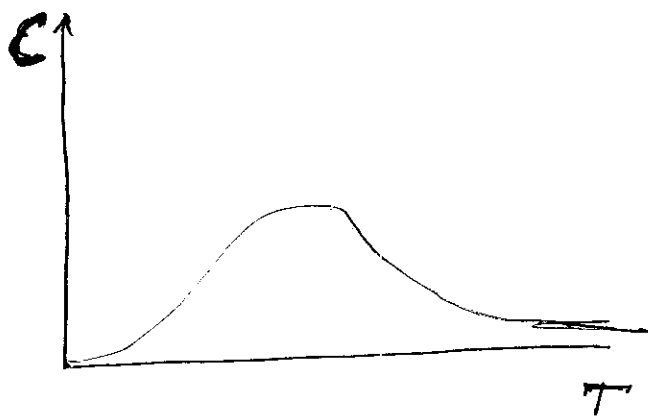
$$T \rightarrow 0, \quad w_1 \rightarrow 1, \quad w_2 \rightarrow 0$$

$$T \rightarrow \infty, \quad w_1 \rightarrow \frac{1}{2}, \quad w_2 \rightarrow \frac{1}{2}$$

$$\bar{E} = 0 \cdot w_1 + \epsilon \cdot w_2 = \frac{\epsilon e^{-\epsilon/kT}}{1 + e^{-\epsilon/kT}}$$



$C = \frac{d\bar{E}}{dT}$ - heat capacity

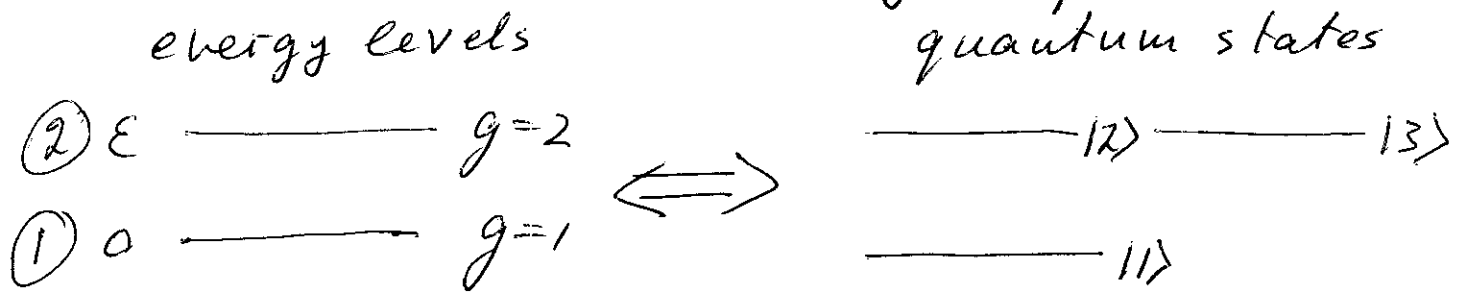


If there are N systems of this type, for example N two-level atoms, then

$$\bar{E} \rightarrow N\bar{E}, \quad \bar{E} = \frac{N\epsilon e^{-\epsilon/kT}}{1 + e^{-\epsilon/kT}}$$

$$C \rightarrow NC,$$

Example II: 2-level system with degeneracy (3 quantum states)



$$Z = \sum_i e^{-\frac{\epsilon_i}{kT}} = e^{-\frac{0}{kT}} + e^{-\frac{\epsilon}{kT}} + e^{-\frac{\epsilon}{kT}} = 1 + 2e^{-\frac{\epsilon}{kT}}$$

$$\left\{ \begin{array}{l} w_1 = \frac{1}{Z} = \frac{1}{1 + 2e^{-\frac{\epsilon}{kT}}} \quad \text{probability to find state } |1\rangle \\ w_2 = \frac{1}{Z} e^{-\frac{\epsilon}{kT}} = \frac{e^{-\frac{\epsilon}{kT}}}{1 + 2e^{-\frac{\epsilon}{kT}}} \quad \text{probability to find state } |2\rangle \\ w_3 = \frac{1}{Z} e^{-\frac{\epsilon}{kT}} = \frac{e^{-\frac{\epsilon}{kT}}}{1 + 2e^{-\frac{\epsilon}{kT}}} \quad \text{probability to find state } |3\rangle \end{array} \right.$$

$$\left\{ \begin{array}{l} P_1 = w_1 \quad - \text{probability to find level 1} \\ P_2 = w_2 + w_3 \quad - \text{probability to find level 2} \end{array} \right.$$

$$w_i = \frac{1}{Z} e^{-\frac{\epsilon_i}{kT}}$$

two equivalent forms
of the Boltzmann
distribution

$$p_i = \frac{1}{Z} g_i e^{-\frac{\epsilon_i}{kT}}$$

g_i is degeneracy

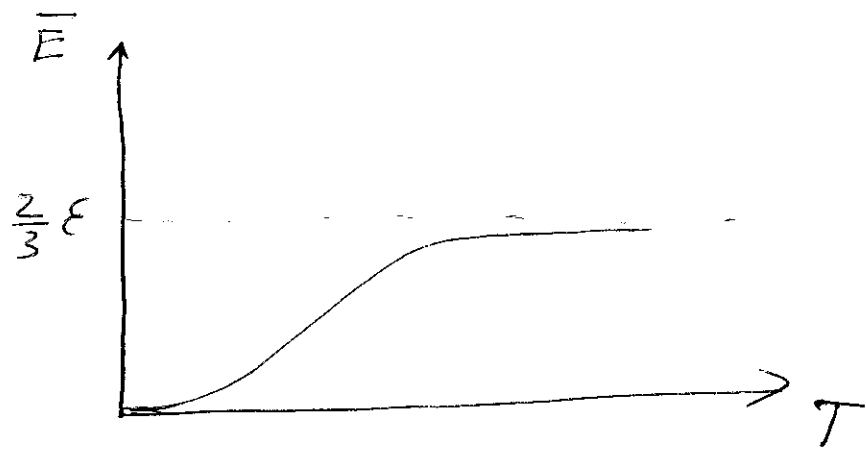
Average energy

$$\bar{E} = \sum_i \epsilon_i w_i = \sum_i \epsilon_i p_i = \frac{2\epsilon e^{-\epsilon/kT}}{1 + 2e^{-\epsilon/kT}}$$

summation over states
summation over levels

$$T \rightarrow 0 \quad \begin{cases} w_1 \rightarrow 1 \\ w_2 = w_3 \rightarrow 0 \end{cases}$$

$$T \rightarrow \infty, \quad w_1 = w_2 = w_3 = \frac{1}{3}$$

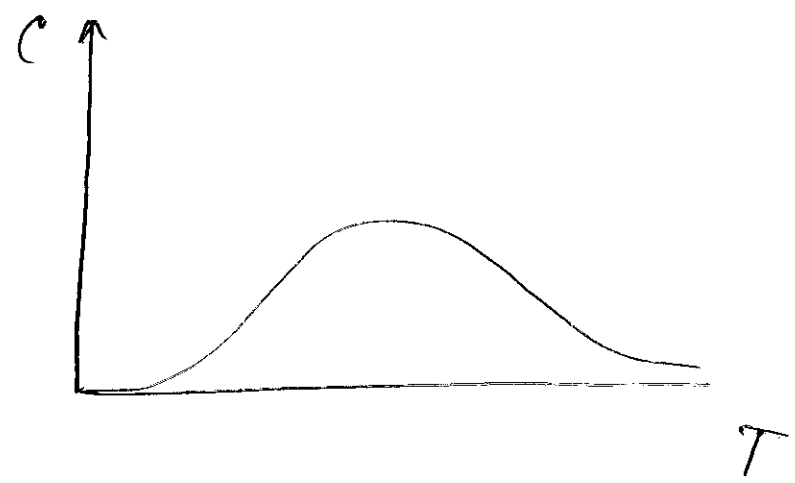


N systems of this type

$$\bar{E} = \frac{N \cdot 2\epsilon e^{-\epsilon/kT}}{1 + 2e^{-\epsilon/kT}}$$

Heat capacity

$$C = \frac{d\bar{E}}{dT}$$



Thermodynamic potentials

(130)

1) Internal energy U has been already discussed

2) Enthalpy H is defined as $H = U + pV$

3) Helmholtz free energy F is defined as $F = U - TS$

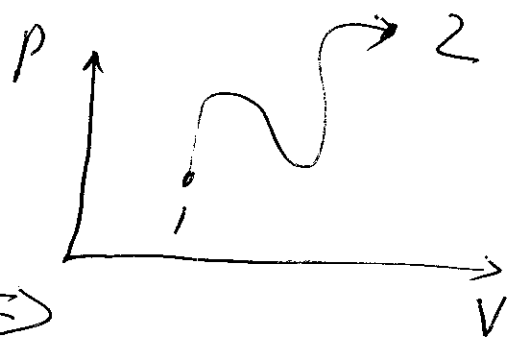
4) Gibbs free energy G is defined as $G = F + pV = U - TS + pV$

Consider any process $1 \rightarrow 2$

1st law: $du = dq - dw$

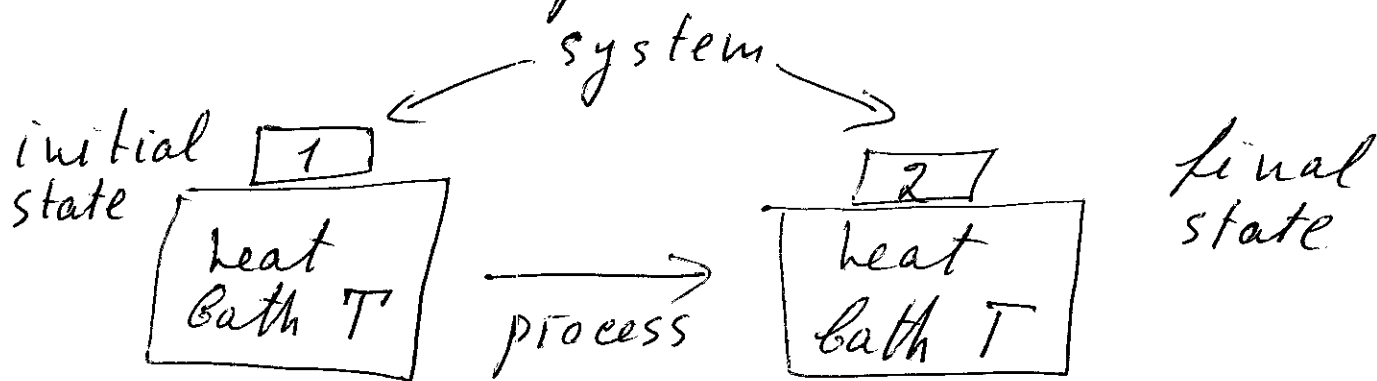
$$\Rightarrow \Delta U = U_2 - U_1 = Q - W \Rightarrow$$

$$\Rightarrow \boxed{W = Q + U_1 - U_2} \quad \text{- work done by the system in the process.}$$



Maximum work

A system undergoes a process between two equilibrium states. Heat flows from a reservoir ^(heat bath) with a given temperature T . Initial and final states of the system are at the same temperature.



S is the entropy of the system
 S_r is the entropy of the reservoir

2nd law of thermodynamics

$$S_2 - S_1 + \Delta S_r \geq 0$$

$\Delta S_r = -\frac{Q}{T}$, where Q is the heat flow into the system.

$$\Rightarrow S_2 - S_1 - \frac{Q}{T} \geq 0 \Rightarrow T(S_2 - S_1) \geq Q$$

from page 130 \Rightarrow

$$W = Q + U_1 - U_2 \leq (U_1 - U_2) - T(S_1 - S_2) \Rightarrow$$

$$W \leq \underbrace{(U_1 - TS_1)}_{F_1} - \underbrace{(U_2 - TS_2)}_{F_2} \Rightarrow \boxed{W \leq F_1 - F_2}$$

arbitrary process

For a reversible process $\Delta S = 0 \Rightarrow$

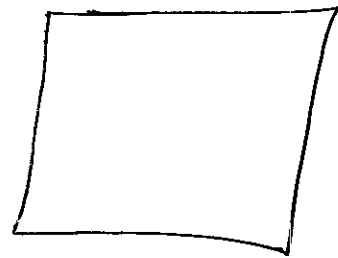
(see page 131)

$$\Rightarrow \boxed{W = F_1 - F_2} - \text{maximum work that can be done by the system.}$$

This equation is also the origin of the term "free energy".

Consider a system with fixed volume

$$dw = pdv = 0$$

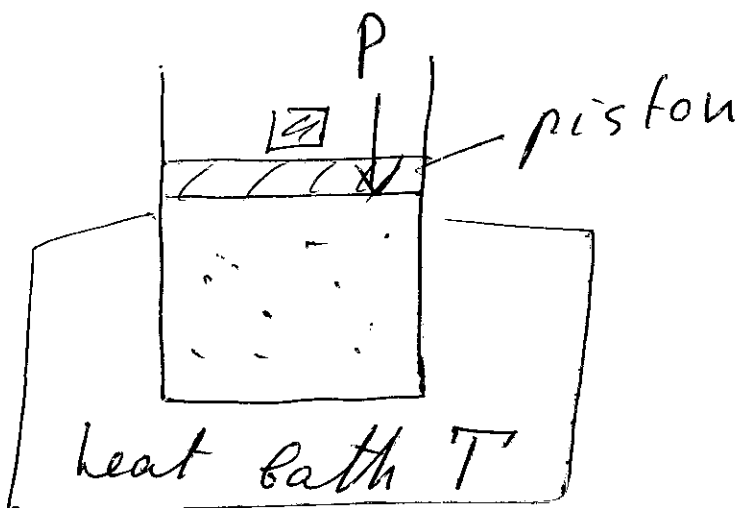


$v = \text{const.}$
 $T = \text{const}$

\Rightarrow $0 \leq F_1 - F_2$ in any process!

\Rightarrow in the equilibrium F takes minimal value
 $T = \text{const}$
 $v = \text{const}$

Consider now a system at a given temperature and at a given pressure



$$w = \int p dv = p(v_2 - v_1)$$

$$p(v_2 - v_1) \leq F_1 - F_2$$

$$0 \leq \underbrace{(F_1 + pV_1)}_{G_1} - \underbrace{(F_2 + pV_2)}_{G_2}$$

$$0 \leq G_1 - G_2$$

in any process at
 $T = \text{const}, p = \text{const}.$

Hence

In the equilibrium at fixed temperature and pressure the Gibbs free energy G takes minimal value.

Example: ideal gas

consider 1 mole of the gas

$$pV = RT,$$

V is the molar volume

U is the molar internal energy

$$U = C_v T, \quad C_v = \frac{i}{2} RT$$

1st law: $T ds = du + p dV$

$$T ds = C_v dT + p dV \Rightarrow$$

$$\Rightarrow ds = C_v \frac{dT}{T} + \frac{p}{T} dV = C_v \frac{dT}{T} + R \frac{dV}{V}$$

integration
→

$$S = C_v \ln \frac{T}{T_0} + R \ln \frac{V}{V_0} + S_0$$

$$\frac{V}{V_0} = \frac{T}{T_0} \frac{P_0}{P} \Rightarrow$$

$$\Rightarrow S = C_v \ln \frac{T}{T_0} + R \ln \frac{T}{T_0} \frac{P_0}{P} =$$

$$= \underbrace{(C_v + R)}_{C_p} \ln \frac{T}{T_0} + R \ln \frac{P_0}{P}$$

$$\Rightarrow S = C_p \ln \frac{T}{T_0} - R \ln \frac{P}{P_0} + S_0$$

$$\frac{T}{T_0} = \frac{V}{V_0} \frac{P}{P_0} \Rightarrow$$

$$S = C_p \ln \frac{V}{V_0} + C_v \ln \frac{P}{P_0} + S_0$$

Adiabatic process: $S = \text{const}$

see page 135

$$\rightarrow C_p \ln V + C_v \ln p = \text{const} \Rightarrow$$

$$\Rightarrow \left(\frac{C_p}{C_v} \right) \ln V + \ln p = \text{const} \Rightarrow$$

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$$\Rightarrow \gamma \ln V + \ln p = \ln V^\gamma p = \text{const} \Rightarrow$$

$$\Rightarrow \boxed{pV^\gamma = \text{const}}$$

molar enthalpy of the ideal gas

$$h = u + pV = C_v T + RT = C_p T$$

molar Gibbs free energy of the gas

$$g = u - TS + pV = h - TS =$$

$$= C_p T - T \left[C_p \ln \frac{T}{T_0} + R \ln \frac{p}{p_0} + S_0 \right]$$

$$\boxed{g = RT \left[\ln p + \varphi(T) \right]}$$

where $\varphi(T)$ depends only on T

$$RT \varphi(T) = C_p T - C_p T \ln \frac{T}{T_0} - RT \ln p_0 - T S_0$$