4. Systems in contact with a thermal bath

So far, isolated systems (micro-canonical methods)

4.1 Constant number of particles: Kittel&Kroemer Chap. 3

- Boltzmann factor
- Partition function (canonical methods)
- Ideal gas (again!)
  - Entropy = Sackur-Tetrode formula
  - Chemical potential

4.2 Exchange of particles: Kittel&Kroemer Chap. 5

- Gibbs Factor
- Grand Partition Function or Gibbs sum
  - (grand canonical methods)
Ideal Gas Thermal Bath

Consider 1 particle in thermal contact with a thermal bath made of an ideal gas with a large number \( M \) of particles.

We assume that the overall system is isolated and in equilibrium at temperature \( \tau \). We call \( U \) the total energy (which is constant).

We would like to compute the probability of having our particle in a state of energy \( \varepsilon \). Because in equilibrium, all states of the overall system are equiprobable, this is equivalent to computing the number of states such that our particle has energy \( \varepsilon \) and the thermal bath \( U-\varepsilon \).

Using the fact that for an ideal gas of energy \( E \) and particle number \( M \), the number of states is

\[ g \propto E^{3/2M} \]

and that

\[ U = \frac{3}{2}(M + 1)\tau \]

We obtain for large \( M \)

\[ \text{prob}(\varepsilon) \propto (U - \varepsilon)^{\frac{3}{2}M} \propto \left(1 - \frac{\varepsilon}{\frac{3}{2}(M + 1)\tau}\right)^{\frac{3}{2}M} \xrightarrow{M \to \infty} \exp\left(-\frac{\varepsilon}{\tau}\right) \]
Boltzmann factor

System in contact with thermal bath (reservoir)

Constant number of particles

Total system = Our system $S$ + reservoir $R$, isolated

\[
\mathcal{R}, U_o - \varepsilon
\]

$S, \varepsilon$

Configuration: 1 state of $S$

+ energy of reservoir

\[
\# \text{States in configuration} = 1 \times g_R(U_o - \varepsilon)
\]

Fundamental postulate: at equilibrium

\[
\text{Prob(configuration)} \propto g_R(U_o - \varepsilon)
\]

\[
\Rightarrow \frac{\text{Prob(state } \varepsilon_1)}{\text{Prob(state } \varepsilon_2)} = \frac{g_R(U_o - \varepsilon_1)}{g_R(U_o - \varepsilon_2)} = \exp(\sigma_R(U_o - \varepsilon_1) - \sigma_R(U_o - \varepsilon_2))
\]

\[
\Rightarrow \frac{\text{Prob(state } \varepsilon_1)}{\text{Prob(state } \varepsilon_2)} = \exp\left(\frac{\partial \sigma_R}{\partial U_o}(\varepsilon_2 - \varepsilon_1)\right) = \exp\left(\frac{1}{\tau}(\varepsilon_2 - \varepsilon_1)\right)
\]

\[
\Leftrightarrow \text{Prob(state } \varepsilon_s) = \frac{1}{Z} \exp\left(-\frac{\varepsilon_s}{\tau}\right) = \frac{1}{Z} \exp\left(-\frac{\varepsilon_s}{k_BT}\right)
\]

with $Z = \sum_{\text{all states } s} \exp\left(-\frac{\varepsilon_s}{\tau}\right)$

Notes:

- $\exp\left(-\frac{\varepsilon_s}{\tau}\right) = \text{Boltzmann factor}$
- $Z$ = partition function
- Probability of each state not identical!

$\Leftrightarrow$ interaction with bath
**Partition Function**

**Definition**

\[ Z = \sum_{\text{all states } s} \exp\left(-\frac{\varepsilon_s}{\tau}\right) \]

If states are degenerate in energy, each one has to be counted separately =>

\[ Z = \sum_{\varepsilon_i} g_i \exp\left(-\frac{\varepsilon_i}{\tau}\right) \text{ with } g_i = \text{ multiplicity of state } \varepsilon_i \]

**Example: 2 state system**

State 1 has energy 0
State 2 has energy \( \varepsilon \)

**Probability**

\[ Pr ob (0) = \frac{1}{1 + \exp\left(-\frac{\varepsilon}{\tau}\right)} \]

\[ Pr ob (\varepsilon) = \frac{\exp\left(-\frac{\varepsilon}{\tau}\right)}{1 + \exp\left(-\frac{\varepsilon}{\tau}\right)} = \frac{1}{1 + \exp\left(-\frac{\varepsilon}{\tau}\right)} \]

\[ \varepsilon \]

\[ 0 \]

**Internal Energy**

\[ U = \langle \varepsilon \rangle = \frac{\varepsilon \exp\left(-\frac{\varepsilon}{\tau}\right)}{1 + \exp\left(-\frac{\varepsilon}{\tau}\right)} = \frac{\exp\left(-\frac{\varepsilon}{\tau}\right)}{\exp\left(-\frac{\varepsilon}{\tau}\right) + 1} \]

**Heat Capacity**

\[ C_v = \left(\frac{dQ}{dT}\right)_{V,N} = \left(\frac{\partial U}{\partial T}\right)_{V,N} = k_b \left(\frac{\partial U}{\partial T}\right)_{V,N} = k_b \left(\frac{\varepsilon}{k_b T}\right)^2 \frac{\exp\left(-\frac{\varepsilon}{k_b T}\right)}{\left(\exp\left(-\frac{\varepsilon}{k_b T}\right) + 1\right)^2} \]

Phys 112 (S2006) 04 Boltzmann-Gibbs
Partition Function

Relation with thermodynamic functions

Energy

\[ U = \langle \varepsilon \rangle = \frac{1}{Z} \sum_s \varepsilon_s \exp \left( - \frac{\varepsilon_s}{\tau} \right) = - \frac{1}{\tau} \frac{\partial \log Z}{\partial\tau} = \tau \frac{\partial \log Z}{\partial\tau} \]

Entropy

\[ \sigma = - \sum_s p_s \log p_s = - \sum_s e^{-\frac{\varepsilon_s}{\tau}} \log \left( \frac{e^{-\frac{\varepsilon_s}{\tau}}}{Z} \right) = \log Z + \frac{U}{\tau} = \frac{\partial (\tau \log Z)}{\partial\tau} \]

Free Energy

\[ F = U - \tau\sigma = - \tau \log Z \]

Chemical potential

\[ \mu = \left. \frac{\partial F}{\partial N} \right|_{\tau, V} = - \tau \frac{\partial \log Z}{\partial N} \]

as implied by the thermodynamic identity

\[ \mu = F - N \left( \frac{\partial F}{\partial N} \right) \]

Summation methods

- Direct e.g. geometric series

\[ \sum_{i=0}^{\infty} r^i = \lim_{m \to \infty} \sum_{i=0}^{m} r^i = \lim_{m \to \infty} \frac{1 - r^{m+1}}{1 - r} = \frac{1}{1 - r} \]

- Few term approximation useful if \( f \) decreases fast

\[ \sum_{i=0}^{\infty} f(i) \approx f(0) + f(1) + f(2) + \ldots \]

- Integral approximation

\[ \sum_{i=0}^{\infty} f(i) \approx \int_0^\infty f(x) \, dx \]
Examples

Energy of a two state system

\[ Z = 1 + \exp \left( -\frac{\varepsilon}{\tau} \right) \]

\[ U = \langle \varepsilon \rangle = \frac{\tau^2 \partial \log Z}{\partial \tau} = \frac{\varepsilon \exp \left( -\frac{\varepsilon}{\tau} \right)}{1 + \exp \left( -\frac{\varepsilon}{\tau} \right)} = \frac{\varepsilon}{\exp \left( \frac{\varepsilon}{\tau} \right) + 1} \]

Free particle at temperature \( \tau \)

Assumption: No additional degrees of freedom
e.g. no spin, not a multi-atom molecule

Method 1: density in phase space

Energy:

\[ \varepsilon = p_x^2 + p_y^2 + p_z^2 \]

\[ Z_1 = \int \frac{d^3 q}{h^3} \frac{d^3 p}{h^3} \exp \left( -\frac{\varepsilon}{\tau} \right) = \frac{V}{h^3} \int_{-\infty}^{\infty} dp_x e^{-\frac{p_x^2}{2M\tau}} \int_{-\infty}^{\infty} dp_y e^{-\frac{p_y^2}{2M\tau}} \int_{-\infty}^{\infty} dp_z e^{-\frac{p_z^2}{2M\tau}} \]

\[ \Rightarrow Z_1 = V \left( \frac{2\pi M \tau}{h^2} \right)^{\frac{3}{2}} = V \left( \frac{M \tau}{2\pi \hbar^2} \right)^{\frac{3}{2}} = V n_Q \quad \text{with} \quad n_Q = \left( \frac{M \tau}{2\pi \hbar^2} \right)^{\frac{3}{2}} \quad \Rightarrow \quad \langle \varepsilon \rangle = \tau^2 \frac{\partial \log Z_1}{\partial \tau} = \frac{3}{2} \tau \]

Method 2: quantum state in a box: see Kittel-Krömer (chapter 3 p 73)

Same result, of course!
Maxwell Distribution

Applies to classical gases in equilibrium with no potential

Start from Boltzmann distribution

\[
\text{Prob (1 particle to be in state of energy } \varepsilon) = \frac{1}{Z_1} \exp \left( -\frac{\varepsilon}{\tau} \right)
\]

with

\[
Z_1 = \int \frac{d^3q}{h^3} \frac{d^3p}{h^3} \exp \left( -\frac{\varepsilon}{\tau} \right) = V \left( \frac{M\tau}{2\pi^2} \right)^{3/2} = VnQ
\]

Probability of finding this particle in volume dV and between \( p \) and \( p + dp \)

\[
= \frac{1}{VnQ} \exp \left( -\frac{\varepsilon}{\tau} \right) \frac{dV d^3p}{h^3}
\]

For \( N \) particles, the volume density between \( p \) and \( p + dp \)

\[
= \frac{N}{VnQ} \exp \left( -\frac{\varepsilon}{\tau} \right) \frac{d^3p}{h^3}
\]

\[
= \frac{n}{nQ} \exp \left( -\frac{\varepsilon}{\tau} \right) \frac{d^3p}{h^3} = n \left( \frac{1}{2\pi M\tau} \right)^{3/2} \exp \left( -\frac{\varepsilon}{\tau} \right) d^3p
\]

Change of variable to velocities: \( p = Mv \)

Probability of finding particle in \( v, v+dv, d\Omega \)

\[
f(v)dv\Omega = n \left( \frac{M}{2\pi\tau} \right)^{3/2} \exp \left( -\frac{Mv^2}{2\tau} \right) v^2dv\Omega
\]

Maxwell distribution

Particle density distribution in velocity space KK chap. 14 p. 392

Note:
1) Could get the factor in front directly as normalization

2) Note that no \( h \) factor!

3) One can easily compute \( \left\langle \frac{Mv^2}{2} \right\rangle = \frac{3}{2} \tau = \frac{3}{2} k_BT \) Equipartition!
Weak interaction limit

2 subsystems in weak interaction:

$\leftrightarrow$ States of subsystems are not disturbed by interaction (just their population)

$\Rightarrow$ Partition functions

Distinguishable systems

Suppose first that we can distinguish each of the individual components of the system: e.g. adsorption sites on a solid, spins in a lattice

For 2 subsystems

$$Z = \sum_{s_1} \sum_{s_2} \exp \left( -\frac{\varepsilon_{s_1} + \varepsilon_{s_2}}{\tau} \right) \Rightarrow Z(1 + 2) = Z(1)Z(2)$$

and for N systems

$$Z(N) = (Z(1))^N$$
**Examples**

**Free energy of a paramagnetic system**

In a magnetic field $B$, $\varepsilon = -mB$ if $m$ is the magnetic moment.

For 1 spin $Z_1 = \exp\left(-\frac{mB}{\tau}\right) + \exp\left(-\frac{mB}{\tau}\right) = 2 \cosh\left(\frac{mB}{\tau}\right)$

For $N$ spins $Z=Z_1^N$ since they are distinguishable

$$Z = 2^N \cosh^N\left(\frac{mB}{\tau}\right)$$

$$\Rightarrow U = \tau^2 \frac{\partial \log Z}{\partial \tau} = -NmB \tanh\left(\frac{mB}{\tau}\right) \Rightarrow \text{Magnetization } M = -\frac{U}{VB} = nm \tanh\left(\frac{mB}{\tau}\right)$$
Indistinguishable Systems

Indistinguishable: in quantum mechanics, free particles are indistinguishable

We should count permutations of states among particles only once
e.g. for 2 particles $Z(1)Z(2) = \sum e^{-\frac{\epsilon_{s_1}}{\tau}} \sum e^{-\frac{\epsilon_{s_2}}{\tau}}$ overcounts $s_1, s_2 \equiv s_2, s_1$ for $s_1 \neq s_2$ we have to divide by 2

More generally if we have $N$ identical systems, the $N$th power of $Z_1$ can be expanded as

$$(a_1 + \ldots + a_s + \ldots a_m)^N = \sum_{n_1 \ldots n_s} \frac{N!}{n_1 ! \ldots n_s ! \ldots n_m !} a_1^{n_1} \ldots a_s^{n_s} \ldots a_m^{n_m}$$

If we have a large number of possible states, most of the terms are of the form $N! a_j a_j \ldots a_k$ corresponding to $N$ different states which are singly occupied. If the multiple occupation of states is negligible we are indeed overcounting by $N!$

Therefore if we have $N$ indistinguishable systems

$$Z(N) \approx \frac{1}{N!} (Z(1))^N$$

This is a low occupation number approximation due to Gibbs

( no significant probability to have 2 particles in the same state: we will see how to treat the case of degenerate quantum gases)
Ideal Gas

**N atoms**

Indistinguishable

\[ Z_N = \frac{1}{N!} (Z_1)^N = \frac{1}{N!} (n_Q V)^N \]

\[ \log N! \approx N \log N - N \Rightarrow \log Z_N = N \log \left( n_Q V \right) + N \]

\[ \log Z_N = N \log \left( \frac{n_Q}{n} \right) + N \]

with \( n = \frac{N}{V} \) = concentration

**Interpretation:** \( n_Q \) as quantum concentration

de Broglie wave length

\[ \lambda = \frac{h}{Mv} \approx \frac{h}{\sqrt{3M\tau}} \ll \frac{1}{2} Mv^2 \approx \frac{3}{2} \tau \]

\[ n_Q \approx \frac{1}{\lambda^3} \approx \left( \frac{3M\tau}{h^2} \right)^{\frac{3}{2}} \approx \left( \frac{M\tau}{2\pi h^2} \right)^{\frac{3}{2}} \]
Ideal gas laws

Energy

\[ U = \frac{1}{2} \tau^2 \frac{\partial \log Z}{\partial \tau} = \frac{3}{2} N \tau = \frac{3}{2} N k_B T \]

equipartition of energy \( \frac{1}{2} \tau \) per degree of freedom

Free energy

\[ F = -\tau \log Z = -\tau N \log \left( \frac{n_Q}{n} \right) - \tau N \]

Pressure

\[ p = -\frac{\partial F}{\partial V} = \frac{\tau N}{V} \Rightarrow pV = N \tau = N k_B T \]

Entropy: Sackur Tetrode

\[ \sigma = \frac{S}{k_B} = -\frac{\partial F}{\partial \tau} = N \left[ \log \left( \frac{n_Q}{n} \right) + \frac{5}{2} \right] \]

identical to our expression counting states

if extra degrees of freedom, additional terms!
Well verified by experiment
Involves quantum mechanics

Chemical potential

\[ \mu = \frac{\partial F}{\partial N} = \tau \log \left( \frac{n}{n_Q} \right) \]
Chemical Potential

Physical Picture

For an ideal gas without an external potential

\[ \mu = \tau \log \left( \frac{n}{n_Q} \right) \]

Concentration!

Constancy of chemical potential = constancy of concentration <=

Diffusion

Wall partially transparent to particles

Initial state

Final state
Internal Degrees of Freedom (Optional)

In general, we need to add internal degrees of freedom.

In most cases, the kinetic and internal degrees of freedom are independent, for one particle, \( Z = Z_{\text{kin}} \cdot Z_{\text{int}} \).

e.g. for multi-atomic molecules

Rotation \( \approx 10^{-2} \text{ eV} \)

Rotation energy \( \varepsilon_j = j(j+1)\varepsilon_0 \) with multiplicity \( 2j+1 \)

\[
Z_{\text{int}} = \sum_j (2j+1) \exp \left( -\frac{j(j+1)\varepsilon_0}{\tau} \right) = \int_{-1/2}^{1/2} (2j+1) \exp \left( -\frac{j(j+1)\varepsilon_0}{\tau} \right) dj
\]

\[
= \frac{\tau}{\varepsilon_0} \int_0^\infty \exp(-x) dx \quad \text{with} \quad x = \frac{j(j+1)\varepsilon_0}{\tau} dj, x_0 = \frac{\varepsilon_0}{4\tau}
\]

\[
\Rightarrow Z_{\text{int}} \approx \frac{\tau}{\varepsilon_0} \exp \left( \frac{\varepsilon_0}{4\tau} \right) \frac{\tau}{\varepsilon_0} \quad \text{for} \quad \tau \gg \varepsilon_0 \Rightarrow C_{\text{rot}} = k_B
\]

For \( \tau < \varepsilon_0 \), keep the first terms of the discrete sum \( Z_{\text{int}} \approx 1 + 3 \exp \left( -2 \frac{\varepsilon_0}{\tau} \right) + ... \)

\[
\log Z_{\text{int}} \approx 3 \exp \left( -2 \frac{\varepsilon_0}{\tau} \right) U = \frac{\tau^2}{\varepsilon_0} \frac{d\log Z}{d\tau} \approx 6 \varepsilon_0 \exp \left( -2 \frac{\varepsilon_0}{\tau} \right) \quad C_{\text{rot}} \approx 12k_B \left( \frac{\varepsilon_0}{\tau} \right)^2 \exp \left( -2 \frac{\varepsilon_0}{\tau} \right) \approx 0
\]

Vibration \( \approx 2 \times 10^{-1} \text{ eV} \) similar to harmonic oscillator

\[
Z_{\text{int}} = \sum_{n=0}^\infty \exp \left( -\frac{nh\omega}{\tau} \right) = \frac{1}{1 - \exp \left( -\frac{h\omega}{\tau} \right)} \approx \frac{\tau}{h\omega} \quad \text{for} \quad \tau \gg h\omega \Rightarrow C_{\text{vib}} = k_B
\]

Spin in a magnetic field etc..
Exchanging Particles with an Ideal gas

Let us consider again a system with an energy level $\varepsilon$, which can now be occupied by a variable number $N$ of particles.

We put in contact with a thermal reservoir constituting on a large number $M-N$ of free particles. Energy and particles can be exchanged with the reservoir.

We consider a single state with $N$ particles and an energy $N\varepsilon$.

We can draw qualitatively the number of states of the overall system as a function of $N$.

$$g = g_{\text{Res}} \times 1 = \left[ e^{5/2} \left( \frac{m}{2\pi \hbar^2} \frac{2U - N\varepsilon}{3(M - N)} \right)^{3/2} \right]^{M-N}$$

Direct Counting or Seckur Tetrode

$$g_{\text{Res}} = \exp \left( -\frac{(\varepsilon - \mu)N}{\tau} \right)$$
Exploration

Let us show that the probability of having \( N \) particles is

\[
prob(\varepsilon, N) = \frac{g}{g_t} \propto \exp \left( -\frac{(\varepsilon - \mu)N}{\tau} \right)
\]

Direct calculation to take into account \( N \) dependence both in exponent and inside the bracket

\[
g = \left[ \left( \frac{m}{2\pi\hbar^2} \frac{2U}{3M} \right)^{3/2} \right]^{M-N} \left[ \left( 1 - \frac{\varepsilon N}{U} \right)^{3/2} \right]^{M-N} \left[ \frac{1}{(1 - \frac{N}{M})} \right]^{3/2} e^{3/2(M-N)}
\]

For \( N \ll M, M \to \infty \) \( U \approx \frac{3}{2} M \tau \left( \frac{m}{2\pi\hbar^2} \frac{2U}{3M} \right)^{3/2} \approx n_Q \left( \frac{M}{V} \right) = n \)

\[
g \approx \left( \frac{n_Q}{n} \right)^{M-N} \exp \left( -\frac{\varepsilon N}{\tau} \right) \frac{1}{\exp \left( -\frac{5}{2} N \right)} e^{3/2(M-N)} \left( e^{3/2} \frac{n_Q}{n} \right)^{M} \exp \left( -\frac{\varepsilon - \tau \log \left( \frac{n}{n_Q} \right)}{\tau} \right) N
\]
Gibbs factor

System in contact with thermal bath (reservoir)

Exchange of particles

\[ R, \ U_o - \varepsilon \]

\( S, \varepsilon \)

# States in configuration

\[ 1 \times g_R(U_o - \varepsilon_s, N_{oi} - N_o) \]

At equilibrium

\[ \Rightarrow \text{Prob}(\text{state } \varepsilon_1, N_{i1}) = g_R(U_o - \varepsilon_1, N_{oi} - N_o) \]

\[ = g_R(U_o - \varepsilon_1, N_{oi} - N_o) \]

\[ = \exp \left( -\frac{\partial \sigma_R}{\partial U} (\varepsilon_1 - \varepsilon_2) - \sum_i \frac{\partial \sigma_R}{\partial N_i} (N_{i1} - N_{i2}) \right) \]

\[ \Leftrightarrow \text{Prob}(\text{state } \varepsilon_s, N_{is}) = \frac{1}{Z} \exp \left( \frac{\varepsilon(s, N_{is}) - \sum_i \mu_i N_{is}}{\tau} \right) = \frac{1}{Z} \exp \left( -\frac{\varepsilon(s, N_{is}) - \sum_i \mu_i N_{is}}{k_B T} \right) \]

with \( Z = \sum_{\text{all states } s, N_{is}} \exp \left( -\frac{\varepsilon(s, N_{is}) - \sum_i \mu_i N_{is}}{\tau} \right) \)

Notes:

- \( Z \) = grand partition function
- Absolute activity \( \lambda_i = \exp \left( \frac{\mu_i}{\tau} \right) \)

Total system = Our system + reservoir

Configuration: 1 state \( s \) of \( S \)

of energy \( \varepsilon_s \) and # of particles \( N_{is} \)

+ energy of reservoir
Grand Partition Function

**Definition**

\[
Z = \sum_{\text{all states } s \text{ and occupation } N_{is}} \exp \left( \frac{\sum_i \mu_i N_{is} - \varepsilon(s, N_{is})}{\tau} \right)
\]

**Note:** \(\varepsilon(s, N)\) depends on \(N_i\) both through increase of \(N\), and the interactions

In weak interaction limit (ideal gas) and only 1 species,

\[
\varepsilon(s, N_s) = N_s \epsilon_s \quad \Rightarrow \quad Z = \sum_{s,N_s} \exp \left( -\frac{(\epsilon_s - \mu)N_s}{\tau} \right)
\]

**Note** If the \(N_{is} = N_i\) are constant,

\[
Z = \exp \left( \frac{\sum_i \mu_i N_{i}}{\tau} \right) Z(N_i)
\]

the probabilities are the same as with \(Z\)

This formalism is useful only if the \(N_{is}\) change.
**Examples** few state systems  

**Gas absorption** *(heme in myoglobin, hemoglobin, walls)*  
Assume that each potential absorption site can absorb at most one gas molecule. What is the fraction of sites which are occupied? 
State 1= 0 molecule => energy 0  
State 2= 1 molecule => energy $\varepsilon$  

$$Z = 1 + \exp\left(\frac{\mu - \varepsilon}{\tau}\right)$$  

Fraction occupied = $$f = \frac{\exp\left(\frac{\mu - \varepsilon}{\tau}\right)}{1 + \exp\left(\frac{\mu - \varepsilon}{\tau}\right)} = \frac{1}{\exp\left(\frac{\varepsilon - \mu}{\tau}\right) + 1}$$  

How is $\mu$ determined? <= gas in equilibrium with absorption sites  

If ideal (applies equally well to gas and dissolved gas)  
Langmuir adsorption isotherm  

$$f = \frac{p}{nQ \exp\left(\frac{\varepsilon}{\tau}\right) + p}$$  

$$\mu_{gas} = \tau \log\left(\frac{n}{nQ}\right) = \tau \log\left(\frac{p}{nQ^{\tau}}\right) \iff pV = N\tau \quad n = \frac{N}{V} = \frac{P}{\tau}$$
Ionized impurities in a semiconductor

**Donor= tends to have 1 more electron** (e.g. P in Si)
- State 1= ionized \( D^+ \): no electron => energy= 0
- State 2=neutral 1 extra electron spin up => energy \( = \varepsilon_d \)
- State 3= neutral 1 extra electron spin down => energy \( = \varepsilon_d \)

\[
\text{Fraction ionized } f = \frac{1}{1 + 2 \exp \left( -\frac{\varepsilon_d - \mu}{\tau} \right)}
\]

\( \varepsilon_d = \text{energy of electron on donor site} \)

K&K use ionization energy \( I = -\varepsilon_d \)

**Acceptor= tends to have 1 fewer electron** (e.g. Al in Si)
- State 1= ionized \( A^- \): one electron completing the bond= energy \( = \varepsilon_a \)
- State 2= 1 neutral: missing a bond electron spin up => energy =0
- State 3= 1 neutral: missing a bond electron spin down => energy =0

\[
\text{Fraction ionized } f = \frac{1}{\exp \left( -\frac{\varepsilon_a - \mu}{\tau} \right) + 2 \exp \left( -\frac{\mu - \varepsilon_a}{\tau} \right)} = \frac{1}{1 + 2 \exp \left( -\frac{\mu - \varepsilon_a}{\tau} \right)}
\]

\( \varepsilon_a = \text{energy of electron on acceptor site} \)

\( \mu = \text{Fermi level} \)

\( \mu \) determined by electron concentration in semiconductor
**Grand Partition Function**

**Relation to thermodynamic functions**

- **Mean number of particles**
  \[
  \langle N_i \rangle = \sum_s \sum_{N_is} N_is P_{s,N_is} = \sum_s \sum_{N_is} N_is \exp \left( \sum_i \frac{\mu_i N_is - \epsilon(s,N_is)}{\tau} \right) = \tau \frac{\partial \log 3}{\partial \mu_i}
  \]

- **Entropy**
  \[
  \sigma = -\sum_s \sum_{N_is} p_{s,N_is} \log(p_{s,N_is}) = \log 3 - \sum_i \frac{\mu_i}{\tau} \langle N_is \rangle + \frac{\langle \epsilon \rangle}{\tau} = \frac{\partial (\tau \log 3)}{\partial \tau}
  \]

- **Energy**
  \[
  U = \langle \epsilon \rangle = \tau^2 \frac{\partial \log 3}{\partial \tau} + \sum_i \mu_i \langle N_i \rangle = \left( \tau^2 \frac{\partial}{\partial \tau} + \sum_i \tau \frac{\partial}{\partial \mu_i} \right) \log 3
  \]

- **Free Energy**
  \[
  F = U - \tau \sigma = -\tau \log 3 + \sum_i \mu_i \langle N_i \rangle \quad G = F + pV
  \]

- **Ω defined as**
  \[
  \Omega \equiv F - \sum_i \mu_i \langle N_i \rangle = -\tau \log 3
  \]
Let us consider two isolated systems in interaction with each other.

If \( \text{concentration}_1 > \text{concentration}_2 \), \( \mu_{\text{int}}_1 > \mu_{\text{int}}_2 \)

But if the systems are in equilibrium, they have to have the same total chemical potential

This means that the only way to maintain the difference of concentration is to give some potential energy to system 2 with respect to system 1

Recall \( U = U_K + N\Phi \Rightarrow \mu = \frac{\partial U(\sigma, V, N)}{\partial N} = \frac{\partial U_K}{\partial N} + \Phi \)

In equilibrium, \( \mu_1 = \mu_2 \Leftrightarrow \mu_{\text{int}}_1 + \Phi_1 = \mu_{\text{int}}_2 + \Phi_2 \)

In practice, if you attempt to prevent an evolution of the concentration, you will have to generate a difference of potential energy.

**Example:** Barometric pressure equation

Let us consider a horizontal slab of gas in the (\( \approx \)constant) gravitational potential of the earth. Assume that atmosphere is isothermal and in equilibrium \( \Rightarrow \) constant total chemical potential

\[
\mu(z) = \mu(0) + mgz = \tau \log \left( \frac{n(z)}{n_Q} \right) + mgz = \text{constant} \quad \Rightarrow n(z) = n_o e^{-\frac{mgz}{\tau}}
\]
Three different ways

\[ \mu = \text{constant} \]

Thermodynamic equilibrium between slabs at various z

At constant temperature \( \mu_{\text{total}} = C \) \( \iff \tau \log \frac{n(z)}{n_0} = -\Phi(z) + C \iff n(z) = n_0 \exp \left( -\frac{mgz}{\tau} \right) \)

Single particle occupancy of levels at different altitude

\[ n(z) \propto \text{prob}(\epsilon_k, z) \propto \exp \left( -\frac{\epsilon_k + \Phi(z)}{\tau} \right) \implies n(z) = n_0 \exp \left( -\frac{mgz}{\tau} \right) \]

Hydrodynamic equilibrium

\[ -(p + dp)dA \]

\[-mg(n(z))dA dz \]

\[ pdA - (p + dp)dA - mg n(z) dAdz = 0 \implies \frac{1}{n(z)} \frac{\partial p}{\partial z} = -mg \]

\[ pV = N\tau \iff p(z) = n(z)\tau \implies \frac{1}{n(z)} \frac{\partial n}{\partial z} = -\frac{mg}{\tau} \]

At a deeper level the constancy of the total chemical potential in a system in equilibrium reflects the balance between the drift current generated by the external potential and the diffusion current due to the random thermal velocity.

cf. Chapter 10 of the notes
Other Examples

Equilibrium across a membrane: Osmotic diffusion

Concentrations across the membrane want to be equal, but the quantity of material can be very different, e.g., reverse osmotic diffusion for desalination.

Ions: interplay of chemistry and electricity

When the cell needs more molecules, trapping sites are generated.
Process continues till most of the sites are occupied. Example: Lungs.

If these molecules are ions, this generates a potential difference with outside.
Process continues till the electric potential difference stops the diffusion.

\[ \tau \log \left( \frac{n_{\text{in}}}{n_{\text{out}}} \right) = -q(V_{\text{in}} - V_{\text{out}}) \]

This would limit the concentration of ions! In order to circumvent the problem, the membrane recognizes the ions and lets them through. This is not thermal equilibrium!

Battery (K&K p.129) Example of mix of chemistry and electricity

Consider an electrolyte AB: ions \( A^- \) \( B^+ \). In the middle of the cell, equilibrium between positive and negative ions.

But on electrodes, selective depletion + repulsion.

\[ \nabla \cdot \vec{E} = \frac{\partial E_z}{\partial z} = \frac{\rho}{\varepsilon \varepsilon_0} \]  

Case where the electrodes are not connected.