5. Systems in contact with a thermal bath

So far, isolated systems (micro-canonical methods)

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

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

5.2 Exchange of particles: Kittel&Kroemer Chap. 5

Gibbs Factor
Grand Partition Function or Gibbs sum
   (grand canonical methods)

5.3 Fluctuations
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 $E = U - \varepsilon$.

Using the fact that for an ideal gas of energy $E$ and particle number $N_p$, the number of states is

$$g \propto E^{3/2N_p}$$

and that

$$U = \frac{3}{2} N_p \tau$$

we obtain for large $N_p$

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

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

$R\ , \ U_o-\varepsilon$

$S, \varepsilon$

Configuration: 1 state of $S$
+ energy of reservoir

# States in configuration

1 $\times \ g_R (U_o - \varepsilon)$

Fundamental postulate (or H theorem): at equilibrium

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

$\Rightarrow \frac{\text{Prob}(\text{state } \varepsilon_1)}{\text{Prob}(\text{state } \varepsilon_2)} = \frac{g_R (U_o - \varepsilon_1)}{g_R (U_o - \varepsilon_2)} = \exp \left( \sigma_R (U_o - \varepsilon_1) - \sigma_R (U_o - \varepsilon_2) \right)$

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

$\Leftrightarrow \text{Prob}(\text{state } \varepsilon_s) = \frac{1}{Z} \exp \left( - \frac{\varepsilon_s}{\tau} \right) = \frac{1}{Z} \exp \left( - \frac{\varepsilon_s}{k_B T} \right)$

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

Notes:

- $\exp \left( - \frac{\varepsilon_s}{\tau} \right) = \text{Boltzmann factor}$

- $Z = \text{partition function}$

- Probability of each state not identical!

- $\triangleleft$ interaction with bath
**Examples**

**2-state system**

State 1 has energy 0
State 2 has energy $\varepsilon$

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

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

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

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

\[
Prob(2) = \frac{\exp\left(\frac{-\varepsilon}{\tau}\right)}{1 + \exp\left(\frac{-\varepsilon}{\tau}\right)} = \frac{1}{1 + \exp\left(\frac{\varepsilon}{\tau}\right)}
\]

\[
Prob(0) \quad \text{Prob}(\varepsilon)
\]

\[
V(N) = k_b \left(\frac{\varepsilon}{k_b T}\right) \left(\frac{\varepsilon}{k_b T}\right) \left(\frac{\varepsilon}{k_b T}\right) + 1
\]
Examples

Free particle at temperature $\tau$

Assumption: No additional degrees of freedom

\[ \text{e.g. no spin, not a multi-atom molecule} \]

\[
\text{Prob}\left(\frac{dV}{\text{volume element}}, \left[\frac{p}{\text{Momentum interval}}, \frac{p + dp}{\text{solid angle element}}\right], \frac{d\Omega}{\text{solid angle element}}\right) = \frac{1}{Z} \exp\left(-\frac{p^2}{2M\tau}\right) \frac{dVp^2dpd\Omega}{h^3} \]

\[ d\Omega = d\cos\theta d\phi \]

\[
= \text{Prob}\left(\frac{dV}{\text{volume element}}, \left[\epsilon, \epsilon + d\epsilon\right], \frac{d\Omega}{\text{solid angle element}}\right) = \frac{\sqrt{2}M^{3/2}}{Z} \exp\left(-\frac{\epsilon}{\tau}\right) \frac{dV\sqrt{\epsilon}d\epsilon d\Omega}{h^3}
\]

\[
= \text{Prob}\left(\frac{dV}{\text{volume element}}, \left[v, v + dv\right], \frac{d\Omega}{\text{solid angle element}}\right) = \frac{M^3}{Z} \exp\left(-\frac{1}{2}\frac{Mv^2}{\tau}\right) \frac{dVv^2dv d\Omega}{h^3}
\]

Maxwell-Boltzmann distribution $\text{KK p 392}$

Normalizing to $N$ particles, the probability to find one particle per unit volume in the velocity interval $dv$ and solid angle $d\Omega$ is

\[ f(v)dv d\Omega = n \left(\frac{M}{2\pi \tau}\right)^{\frac{3}{2}} \exp\left(-\frac{Mv^2}{2\tau}\right) v^2 dv d\Omega \quad \text{with} \quad n = \frac{N}{V} \]
Another interpretation of the Boltzmann Distribution

We derived it from number of states in the Reservoir

But each excitation in the reservoir will have a typical energy $\approx \tau$

Thermal fluctuations of the order of $\tau$

Difficult to get $\varepsilon \gg \tau$

$$\text{Prob} \propto \exp \left( -\frac{\varepsilon}{\tau} \right)$$
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.

Relation with thermodynamic functions

Energy

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

Entropy

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

Free Energy

\[ F = U - \tau \sigma = -\tau \log Z \quad \Rightarrow \quad \sigma = -\frac{\partial F}{\partial \tau} \quad U = \tau^2 \frac{\partial \log Z}{\partial \tau} = -\tau^2 \frac{\partial \left(\frac{F}{\tau}\right)}{\partial \tau} \]

as implied by the thermodynamic identity

Chemical potential

\[ \mu = \frac{\partial F}{\partial N} \bigg|_{\tau,V} = -\tau \frac{\partial \log Z}{\partial N} \]
Examples

Energy of a two state system

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

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:
\[ \epsilon = \frac{p_x^2 + p_y^2 + p_z^2}{2M} \]
\[ Z_1 = \int \frac{d^3q}{h^3} \frac{d^3p}{h^3} \exp\left(-\frac{\epsilon}{\tau}\right) = \frac{V}{h^3} \int_{-\infty}^{\infty} dp_x e^{-\frac{p_x^2}{2\tau m}} \int_{-\infty}^{\infty} dp_y e^{-\frac{p_y^2}{2\tau m}} \int_{-\infty}^{\infty} dp_z e^{-\frac{p_z^2}{2\tau m}} = \sqrt{2\pi\tau m} \]
\[ \Rightarrow Z_1 = V\left(\frac{2\pi M\tau}{h^2}\right)^{\frac{3}{2}} = V\left(\frac{M\tau}{2\pi h^2}\right)^{\frac{3}{2}} = Vn_Q \quad \text{with} \quad n_Q = \left(\frac{M\tau}{2\pi h^2}\right)^{\frac{3}{2}} \quad \Rightarrow \langle \epsilon \rangle = \tau^2 \frac{\partial \log Z_1}{\partial \tau} = \frac{3}{2} \frac{\tau}{\tau} \]

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

Same result, of course!
Partition Function

Power comes from 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

- Integral approximation
  \[ \sum_{i=0}^{\infty} f(i) = f(0) + f(1) + f(2) + \ldots \]
  \[ \sum_{i=0}^{\infty} f(i) \approx \int_{0}^{\infty} f(x) dx \]

Other example: Harmonic oscillator

Consider an harmonic oscillator \( \hbar \omega \)

The probability of mode of energy \( s\hbar \omega \), \( s \) integer \( \geq 0 \) is

\[ \text{Prob}(s) = \frac{1}{Z} \exp \left( -\frac{s\hbar \omega}{\tau} \right) \]

\[ Z = \sum_{s=0}^{\infty} \exp \left( -\frac{s\hbar \omega}{\tau} \right) = \frac{1}{1 - \exp \left( -\frac{\hbar \omega}{\tau} \right)} \Rightarrow \]

\[ U = \langle s\hbar \omega \rangle = \tau^2 \frac{\partial \log(Z)}{\partial \tau} = \frac{\hbar \omega}{\exp \left( \frac{\hbar \omega}{\tau} \right) - 1} \]
Maxwell Distribution  K&K p. 392

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

Probability of finding this particle in volume dV and between \[\bar{p} \text{ and } \bar{p} + d\bar{p} = \frac{1}{V n_Q} \exp\left(-\frac{\varepsilon}{\tau}\right) \frac{dVd^3p}{h^3}\]

For \(N\) particles, the volume density between \[\bar{p} \text{ and } \bar{p} + d\bar{p} = \frac{N}{V n_Q} \exp\left(-\frac{\varepsilon}{\tau}\right) \frac{d^3p}{h^3}\]

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

Change of variable to velocities: \[p = Mv\]

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

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

Maxwell distribution

Particle density distribution in velocity space

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

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

3) One can easily compute \[\left\langle \frac{Mv^2}{2} \right\rangle = \frac{3}{2} \tau = \frac{3}{2} k_B T\]  Equipartition!
Density of States

Individual States of probability $p_s$

$$\varepsilon \quad \quad \quad \quad \quad \quad \varepsilon + d\varepsilon \quad \quad \quad \quad \quad \quad \varepsilon$$

$$D(\varepsilon)d\varepsilon$$

It is convenient to replace expressions such as $\sum_s p_s f_s$ ($f_s$ any function of the state $s$)

by an integral over the energy $\varepsilon : \sum_s p_s f_s \approx \int_0^\infty p_s(\varepsilon) f_s(\varepsilon) D(\varepsilon) d\varepsilon$

$D(\varepsilon)d\varepsilon$ is the number of states between $\varepsilon$ and $\varepsilon + d\varepsilon$ and is called the density of states.

We replace $\sum_s p_s$ by $p_s(\varepsilon) D(\varepsilon) d\varepsilon$ since for small enough $d\varepsilon$, $p_s$ does not vary

Note that if you ask what is the probability $p(\varepsilon)d\varepsilon$ for the system to be between energy between $\varepsilon$ and $\varepsilon + d\varepsilon$

$$p(\varepsilon)d\varepsilon = p_s(\varepsilon) D(\varepsilon) d\varepsilon$$

i.e., $p(\varepsilon) \neq p_s(\varepsilon)$

For example, for Boltzmann distribution and a non relativistic ideal gas (monoatomic, spinless)

$$p_s(\varepsilon) = \frac{1}{Z} \exp\left(-\frac{\varepsilon}{\tau}\right) \quad \text{and using } p = \sqrt{2M\varepsilon}$$

$$d^3p = p^2 dp d\cos \theta d\phi = p^2 dp d\Omega$$

$$D(\varepsilon)d\varepsilon = \frac{\int_V d^3x \int_{\text{angles}} d\Omega \ p^2 dp}{\hbar^3} = \frac{V 4\pi}{\hbar^3} p^2 \frac{dp}{d\varepsilon} d\varepsilon = \frac{V 4\pi}{\hbar^3} \frac{1}{2} (2M)^{3/2} \sqrt{\varepsilon} d\varepsilon = \frac{V}{4\pi^2} \left(\frac{2M}{\hbar}\right)^{3/2} \sqrt{\varepsilon} d\varepsilon$$
Weak interaction limit

2 sub systems in weak interaction:
<>States of subsystems are not disturbed by interaction (just their population)
<> \( \Psi_{1+2}(n_1, n_2) = \Psi_1(n_1)\Psi_2(n_2) \) with \( n_1, n_2 \) still meaningfull

=> Partition functions multiply for distinguishable systems

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

\[
Z(N) = (Z(1))^N
\]
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

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

$$\Rightarrow U = \tau^2 \frac{\partial \log Z}{\partial \tau} = -N mB \tanh\left(\frac{mB}{\tau}\right) \Rightarrow \text{Magnetization} \ M = -\frac{U}{VB} = n m \tanh\left(\frac{mB}{\tau}\right)$$
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 \( Z(1)Z(2) = \sum_{s_1} e^{-\frac{\varepsilon_{s_1}}{\tau}} \sum_{s_2} e^{-\frac{\varepsilon_{s_2}}{\tau}} \) 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

\[
(a_1 + \ldots + a_s + \ldots a_m)^N = \sum_{n_1, n_2, \ldots} \frac{N!}{n_1! n_2! \ldots} a_1^{n_1} a_2^{n_2} \ldots a_m^{n_m}
\]

If we have a large number of possible states, most of the terms are of the form \( N!a_i a_j \ldots a_k \)

N terms

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

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

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

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

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

\[ n_Q = \left( \frac{M \tau}{2 \pi \hbar^2} \right)^{\frac{3}{2}} \]

Interpretation: \( n_Q \) as quantum concentration

de Broglie wave length

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

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

Energy

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

equipartition of energy \(1/2\tau\) 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

\[ S = \int_0^T \frac{dQ}{T} \]

Chemical potential

\[ \mu = \frac{\partial F}{\partial N} = \frac{\partial}{\partial N} \left( -\tau N \log \left( \frac{n_Q V}{N} \right) - \tau N \right) = \tau \log \left( \frac{n}{n_Q} \right) \]
Barometric Equation: Three different ways

\( \mu = \text{constant} \)

Thermodynamic equilibrium between slabs at various \( z \)

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

Single particle occupancy of levels at different altitude

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

Hydrodynamic equilibrium

\[ - (p + dp) dA \\
- pA \\
- mg \varepsilon(z) dA dz \]

\[ p \, dA - (p + dp) dA - mg \varepsilon(z) dA dz = 0 \quad \Rightarrow \quad \frac{1}{n(z)} \frac{\partial n}{\partial z} = -mg \]

\[ pV = N \tau \quad \Leftrightarrow \quad p(z) = n(z) \tau \quad \Rightarrow \quad \frac{1}{n(z)} \frac{\partial n}{\partial z} = - \frac{mg}{\tau} \]

Generalizes to case when the temperature is not constant
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 \( Z = Z_{\text{kin}} Z_{\text{int}} \).

e.g. for multi-atomic molecules

Rotation \( \approx 10^{-2} \text{ eV} \)
Rotation energy \( \varepsilon_j = j(j + 1)\varepsilon_0 \) with multiplicity \( 2j+1 \)

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

\[
= \frac{\tau}{\varepsilon_0} \int x \exp(-x) dx \quad \text{with} \quad x = \frac{j(j+1)\varepsilon_0}{\tau}
\]

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

For \( \tau < \varepsilon_0 \), keep the first terms of the discrete sum

\[
\log Z_{\text{int}} \approx 3 \exp \left( -\frac{2\varepsilon_0}{\tau} \right) + \ldots
\]

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

Diatomic molecules

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

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 \( N_p - N \) 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 compute the number of states of the overall system as a function of \( N \) and \( \varepsilon \).

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

\[
\lim_{N_p \to \infty} \left[ e^{5/2} \frac{n_0}{n} \right]^{N_p} \exp \left( -N \log \frac{n_0}{n} \right) \exp \left( -\frac{N \varepsilon}{\tau} \right) \approx \exp \left( -\frac{N \varepsilon - \mu}{\tau} \right) \quad \lim_{N \to \infty} \left( 1 + \frac{a}{N} \right)^N = \exp(a)
\]

\[
b^N \equiv \exp(-N \log b)
\]

Phys 112 (S2009) 05 Boltzmann-Gibbs
Gibbs factor

System in contact with thermal bath (reservoir)

Exchange of particles

\[ R, U_o - \varepsilon \]

\[ S, \varepsilon \]

\[ \text{Total system} = \text{Our system} + \text{reservoir} \]

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

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

+ energy of reservoir

\[ \text{# States in configuration} \]

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

At equilibrium

\[ \begin{align*}
    \text{Prob}(\text{state } \varepsilon_1, N_{i1}) &= \frac{g_R(U_o - \varepsilon_1, N_{oi} - N_{i1})}{g_R(U_o - \varepsilon_2, N_{oi} - N_{i2})} \\
    &= \exp \left( -\frac{\partial \sigma_R(U_o - \varepsilon_s,N_{oi} - N_{is})}{\partial U}(\varepsilon_1 - \varepsilon_2) - \sum_i \frac{\partial \sigma_R(N_{i1} - N_{i2})}{\partial N_i} \right) \\
\end{align*} \]

\[ \Leftrightarrow \text{Prob( state } s \text{ with } \varepsilon, N_{is}) = \frac{1}{3} \exp \left( -\sum_i \frac{\varepsilon(s,N_{is}) - \sum \mu_i N_{is}}{\tau} \right) = \frac{1}{3} \exp \left( -\sum_i \frac{\varepsilon(s,N_{is}) - \sum \mu_i N_{is}}{k_B T} \right) \]

with \( 3 = \sum_{\text{all states } s,N_{is}} \exp \left( -\sum_i \frac{\varepsilon(s,N_{is}) - \sum \mu_i N_{is}}{\tau} \right) \)

Absolute activity \( \lambda_i = \exp(\frac{\mu_i}{\tau}) \)

Notes: \[ \cdot 3 = \text{grand partition function} \]
**Grand Partition Function**

**Definition**

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

**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,

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

\[ \text{Prob}(N_s \text{ particles in state } s) = \frac{1}{Z} \exp \left( -\frac{(\varepsilon_s - \mu)N_s}{\tau} \right) \]

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

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

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

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

**Gas adsorption** (heme in myoglobin, hemoglobin, walls)

Assume that each potential adsorption site can adsorb 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 $\varepsilon$

$$3 = 1 + \exp\left(\frac{\mu - \varepsilon}{\tau}\right)$$

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

If ideal (applies equally well to gas and dissolved gas and any low concentration species)

$$\mu_{gas} = \tau \log\left(\frac{n}{nQ}\right) = \tau \log\left(\frac{p}{\tau nQ}\right) \iff pV = N\tau \quad n = \frac{N}{V} = \frac{P}{\tau}$$

Langmuir adsorption isotherm

$$f = \frac{p}{\tau nQ \exp\left(\frac{\varepsilon}{\tau}\right) + p}$$
# Ionized impurities in a semiconductor

*cf* Kittel and Kroemer p370

**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 =\(\varepsilon_d\)

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

\(\varepsilon_d = \) 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= neutral: missing a bond electron spin up => energy =0
State 3= neutral: missing a bond electron spin down => energy =0

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

\(\varepsilon_a = \) energy of electron on acceptor site

\(\mu = \) determined by electron concentration in semiconductor

\(=\) Fermi level
Grand Partition Function

Relation to thermodynamic functions

• Mean number of particles
  \[ \langle N_i \rangle = \sum_s \sum_{N_{is}} N_{is} p_{s,N_{is}} = \sum_s \sum_{N_{is}} \frac{N_{is}}{\tilde{Z}} \exp \left( \frac{\sum_i \mu_i N_{is} - \varepsilon(s,N_{is})}{\tau} \right) = \tau \left. \frac{\partial \log \tilde{Z}}{\partial \mu_i} \right|_{\tau,V} \]

• Entropy
  \[ \sigma = -\sum_s \sum_{N_{is}} p_{s,N_{is}} \log \left( p_{s,N_{is}} \right) = \log \tilde{Z} - \sum_i \frac{\mu_i}{\tau} \langle N_i \rangle + \frac{\langle \varepsilon \rangle}{\tau} = \left. \frac{\partial (\tau \log \tilde{Z})}{\partial \tau} \right|_{V,\mu_i} \]

• Energy
  \[ U = \langle \varepsilon \rangle = \tau^2 \left. \frac{\partial \log \tilde{Z}}{\partial \tau} \right|_{V,\mu_i} + \sum_i \mu_i \langle N_i \rangle = \left( \tau^2 \left. \frac{\partial}{\partial \tau} \right|_{V,\mu_i} + \sum_i \tau \mu_i \left. \frac{\partial}{\partial \mu_i} \right|_{V,\mu_i} \right) \log \tilde{Z} \]

• Free Energy
  \[ F = U - \tau \sigma = -\tau \log \tilde{Z} + \sum_i \mu_i \langle N_i \rangle \quad G = F + pV \]

• Grand Potential \( \Omega \) defined as
  \[ \Omega = F - \sum_i \mu_i \langle N_i \rangle = -\tau \log \tilde{Z} \]
**Fluctuations**

**Microscopic exchanges**

In a system in equilibrium, exchanges still go on at the microscopic level! They are just balanced!

Macroscopic quantities = sum of microscopic quantities

\[ U = \langle \epsilon \rangle = \sum_s \epsilon_s p_s = \sum_s \frac{\frac{\epsilon_s}{\tau}}{Z} \]

But with a finite system, relative fluctuations on such sum is of the order \(1/\sqrt{N}\)

**e.g., fluctuation on total energy**

\[ \sigma_E^2 = \langle (E - \langle E \rangle)^2 \rangle = \langle E^2 \rangle - \langle E \rangle^2 = \sum_s \frac{\epsilon_s^2}{\tau} \frac{e^{\frac{-\epsilon_s}{\tau}}}{Z} - \left( \sum_s \frac{-\epsilon_s}{\tau} \frac{e^{\frac{-\epsilon_s}{\tau}}}{Z} \right)^2 \]

Computation with partition function: By substitution we can see that

\[ \sigma_E^2 = \frac{\tau^2 \partial \log Z}{\partial \tau} \]

Similarly when there is exchange of particles

\[ \langle N \rangle = \frac{\tau \partial \log Z}{\partial \mu} \Bigg|_{\mu,\tau} \text{ and } \sigma_N^2 = \langle N^2 \rangle - \langle N \rangle^2 = \frac{\tau \partial \langle N \rangle}{\partial \mu} = \tau \partial \langle N \rangle \]
Examples

Fermi Dirac

Fermions = particles with half integer spin
Pauli exclusion principle: each state contains at most one particle

For a state of energy $\epsilon$

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

$$\langle N \rangle = \frac{\tau \partial \log Z}{\partial \mu} \bigg|_{\tau \nu} = \frac{\exp \left( -\frac{\epsilon - \mu}{\tau} \right)}{1 + \exp \left( -\frac{\epsilon - \mu}{\tau} \right)} = \frac{1}{\exp \left( \frac{\epsilon - \mu}{\tau} \right) + 1} = \text{Prob}(1 \text{ particle})$$

$$\sigma_N^2 = \frac{\tau \partial \langle N \rangle}{\partial \mu} = \frac{\exp \left( \frac{\epsilon - \mu}{\tau} \right)}{\left[ \exp \left( \frac{\epsilon - \mu}{\tau} \right) + 1 \right]^2} = \langle N \rangle \left( 1 - \langle N \rangle \right) \leq \langle N \rangle$$

Less fluctuation than a Poisson distribution
**Examples**

**Bose Einstein**

Bosons = particles with integer spin

For a state of energy $\varepsilon$

$$Z = \sum_{N} \exp \left( - \frac{[\varepsilon - \mu]N}{\tau} \right) = \frac{1}{1 - \exp \left( - \frac{\varepsilon - \mu}{\tau} \right)}$$

$$\langle N \rangle = \left. \frac{\tau \partial \log Z}{\partial \mu} \right|_{\tau, V} = \frac{\exp \left( - \frac{\varepsilon - \mu}{\tau} \right)}{1 - \exp \left( - \frac{\varepsilon - \mu}{\tau} \right)} = \frac{1}{\exp \left( \frac{\varepsilon - \mu}{\tau} \right) - 1}$$

$$\sigma_N^2 = \left. \frac{\tau \partial \langle N \rangle}{\partial \mu} \right| = \frac{\exp \left( \frac{\varepsilon - \mu}{\tau} \right)}{\left[ \exp \left( \frac{\varepsilon - \mu}{\tau} \right) - 1 \right]^2} = \langle N \rangle \left( 1 + \langle N \rangle \right) \leq \langle N \rangle \quad \text{More fluctuation than a Poisson distribution}$$
Minimization of the Free Energy

Consider a system in interaction with reservoir imposing temperature

Constant exchange of energy (+ in some case volume, particles)

=> Fluctuations, probability distribution

Contrary to a system which is able to loose energy to vacuum, system does not evolve to state of minimum energy (constantly kicked)!

Contrary to an isolated system, does not evolves to a configuration of maximum entropy! (The entropy of the combination of the reservoir and the system is maximized)

It evolves to a configuration of minimum Free Energy

“Balance between tendency to loose energy and to maximize entropy.”

More rigorously

We cannot define the temperature of the system out of equilibrium. So we introduce

\[ F_L(U_S) = U_S - \tau_R \sigma_S(U_S) \] Landau Free Energy (constant volume)

\[ G_L(U_S,V_S) = U_S - \tau_R \sigma_S(U_S,V_S) + p_R V_S \] Landau Free Enthalpy (constant pressure)

They are minimized for the most probable configuration(≈equilibrium)! Can be generalized to any variable! (Will be useful for phase transitions)
Landau Free Energy

Let us consider a system $S$ exchanging energy with a large reservoir $R$. (We are no more considering a single state for system $S$).

Constant volume

$$\sigma_{\text{tot}}(U_S) = \sigma_R(U - U_S) + \sigma_S(U_S)$$

$$= \sigma_R(U) - \frac{1}{U} \sigma_R(U_S) + \sigma_S(U_S)$$

$$= \sigma_R(U) - \frac{1}{\tau_R} U_S + \sigma_S(U_S)$$

$$= \sigma_R(U) - \frac{1}{\tau_R} F_L(U_S) \text{ with}$$

$$F_L(U_S) \equiv U_S - \tau_R \sigma_S(U_S) \equiv \text{Landau Free Energy}$$

Most probable configuration maximizes $\sigma_{\text{tot}}$, i.e., minimizes $F_L(U_S)$

Note that this implies

$$\frac{\partial F_L(U_S)}{\partial U_S} = 0 \iff \frac{\partial \sigma_S(U_S)}{\partial U_S} = \frac{1}{\tau_R}$$

e.g., for a perfect gas

$$\sigma_S(U_S) = N \left\{ \log \left[ \frac{M U_S}{3 \pi h^2 N} \right]^{3/2} + \frac{5}{2} \right\}$$

(Sackur Tetrode with $\tau_S = \frac{2 U_S}{3N}$)

$$\Rightarrow U_S = \frac{3}{2} N \tau_R$$
Exchange of Particles

If we exchange particles, what is minimized is in a way similar to the previous slide

\[ \Omega_L(U_S, N_S) \equiv U_S - \tau_R \sigma_S(U_S, N_S) - \mu_R N_S \]

Landau Grand Potential

in a way similar to the previous slide

\[
\sigma_{tot}(U_S, N_S) = \sigma_R(U - U_S, N - N_S) + \sigma_S(U_S, N_S) \\
= \sigma_R(U) - \frac{\partial \sigma_R}{\partial U} U_S - \frac{\partial \sigma_R}{\partial N} N_S + \sigma_S(U_S, N_S) \\
= \sigma_R(U) - \frac{1}{\tau_R} U_S + \frac{\mu_R}{\tau_R} N_S + \sigma_S(U_S, N_S) \\
= \sigma_R(U) - \frac{1}{\tau_R} \Omega_L(U_S, N_S) \text{ with}
\]

Most probable configuration maximizes \( \sigma_{tot} \) i.e. minimizes \( \Omega_L(U_S, N_S) \)

Note that this implies

\[
\frac{\partial \Omega_L(U_S, N_S)}{\partial U_S} = 0 \iff \frac{\partial \sigma_S(U_S, N_S)}{\partial U} = \frac{1}{\tau_R} \frac{\partial \Omega_L(U_S, N_S)}{\partial N_S} = 0 \iff \frac{\partial \sigma_S(U_S, N_S)}{\partial N_S} = -\frac{\mu_R}{\tau_R}
\]