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
A System in Contact with a Reservoir

The system+ reservoir are isolated and in equilibrium

The system is in one state of energy $\varepsilon$

How does the number of states of the reservoir evolves when $\varepsilon$ increases?
A System in Contact with a Reservoir

The system+ reservoir are isolated and in equilibrium

The system is in one state of energy $\varepsilon$

How does the number of states of the reservoir evolves when $\varepsilon$ increases?

A: Increases
B: Decreases
C: It depends on the conditions
A System in Contact with a Reservoir

The system+ reservoir are isolated and in equilibrium

The system is in one state of energy $\epsilon$

How does the number of states of the reservoir evolves when $\epsilon$ increases?

B: Decreases (very fast)

The total energy is $U_0 = U + \epsilon = \text{Constant} \Rightarrow U = U_0 - \epsilon$
A System in Contact with a Reservoir

The system plus reservoir are isolated and in equilibrium.

How does probability for the system to be in a state of energy $\varepsilon$ vary with $\varepsilon$?
A System in Contact with a Reservoir

The system+ reservoir are isolated and in equilibrium

How does probability for the system to be in a state of energy $\varepsilon$ varies with $\varepsilon$?

A: Increases when $\varepsilon$ increases
B: Decreases when $\varepsilon$ increases
C: Is constant when $\varepsilon$ increases
A System in Contact with a Reservoir

\[ R, U \]

\[ S, \varepsilon \]

The system + reservoir are isolated and in equilibrium

How does probability for the system to be in a state of energy \( \varepsilon \) varies with \( \varepsilon \)?

B: Decreases (very fast)

The probability of having the system in a state of energy \( \varepsilon \) and the reservoir at an energy \( U = U_0 - \varepsilon \)

is proportional to the number of states \( g_R(U_0 - \varepsilon) \times 1 \)
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 $E=U-\varepsilon$.

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 $N_p$

$$\text{prob}(\varepsilon) \propto (U - \varepsilon)^{\frac{3}{2} N_p} \propto \left(1 - \frac{\varepsilon}{\frac{3}{2} N_p \tau}\right)^{\frac{3}{2} N_p} \rightarrow \exp\left(-\frac{\varepsilon}{\tau}\right)$$
Boltzmann factor

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

Total system = Our system \( S \) + reservoir \( \mathcal{R} \), isolated

\[ g_R (U_o - \varepsilon) \]

Configuration: 1 state of \( S \) 
+ energy of reservoir

# States in configuration

1 × \( g_R (U_o - \varepsilon) \)

Fundamental postulate (or H theorem): at equilibrium

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

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

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

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

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

Notes:

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

\[ \Leftarrow \text{interaction with bath} \]
**Examples**

**2-state system**

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

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

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

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

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

\[
\text{Prob}(0) \quad \text{Prob}(\varepsilon)
\]
A System in Contact with a Reservoir

\[ R, U \]

\[ S, \varepsilon \]

The system + reservoir are isolated and in equilibrium

Why does the probability that S in a quantum state energy \( \varepsilon \) decreases exponentially with \( \varepsilon \)?
In class

**A System in Contact with a Reservoir**

\[ \mathcal{R}, U, S, \varepsilon \]

The system + reservoir are isolated and in equilibrium

Why does the probability that \( S \) in a quantum state energy \( \varepsilon \) decreases exponentially with \( \varepsilon \)?

A: Because as you increase \( \varepsilon \), the energy and the number of states in the reservoir increases

B: Because as you increase \( \varepsilon \), the energy of the reservoir decreases and the number of states in the reservoir increases

C: Because as you increase \( \varepsilon \), the energy and the number of states in the reservoir decreases
A System in Contact with a Reservoir

\[ R, U, S, \epsilon \]

The system+ reservoir are isolated and in equilibrium

Why does the probability that \( S \) in a quantum state energy \( \epsilon \) decreases exponentially with \( \epsilon \)?

C: Because as you increase \( \epsilon \), the energy and the number of states in the reservoir decreases

\[ U_R = U_0 - \epsilon \]

\[ g(R) = \text{quickly increasing function of } U_R \]

\[ \text{e.g., ideal gas } \propto U_R^{3/2N} \]
**Examples**

**Free particle at temperature \( \tau \)**

**Assumption:** No additional degrees of freedom  
\( \text{e.g. no spin, not a multi-atom molecule} \)

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

This Boltzmann factor does not vary appreciably over \( dp \)  
\( \text{number of spatial quantum states in phase space element} \)

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

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

**Maxwell-Boltzmann distribution**  
\( KK \, p \, 392 \)

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

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

Why does the Maxwell distribution have a $v^2$

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

Why does the Maxwell distribution has a $v^2$

$$f(v)dv\Omega = n\left(\frac{M}{2\pi\tau}\right)^{\frac{3}{2}} \exp\left(-\frac{Mv^2}{2\tau}\right)v^2dv\Omega \text{ with } n = \frac{N}{V}$$

A: This has to do with the number of states in the reservoir
B: The density of quantum states per unit velocity interval in the system $S$ goes to zero as $v^2$ when $v$ goes to zero
C: This comes from the normalization
In class

Maxwell Distribution

Why does the Maxwell distribution have a $v^2$?

B: The density of quantum states per unit velocity interval in the system $S$ goes to zero as $v^2$ when $v$ goes to zero.

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

- $N = 1$
- $M = 1$
- $\tau = 1$

integrated over angles
Maxwell Distribution

Why doesn't the system $S$ have a fixed energy?
Why doesn’t the system $S$ have a fixed energy?

Which statement is the most accurate

A: The system is not isolated

B: The uncertainty principle prevents this

C: The reservoir keeps “kicking” the system $S$

D: There is constant exchange of energy between $S$ and the reservoir, and the typical energy of these exchanges is $\tau$
Why doesn't the system $S$ have a fixed energy?

The most accurate statement is D

D: There is constant exchange of energy between $S$ and the reservoir, and the typical energy of these exchanges is $\tau$

Example: System $S$ is one particle in a bath of $N$ particles
The average particle energy is $\frac{3}{2}\tau$, and in collisions the typical energy exchanged is a fraction of this.

More general: Energy exchange by various excitations
- Particle collision
- Electrons = Fermi Dirac bath, “electron-like” and “hole-like” excitations $\varepsilon \approx \tau$
- Photons
- Phonons (quantized vibrations in a solid)
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 $\varepsilon >> \tau$

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

**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**

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

**Free Energy**

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

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

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

Free particle at temperature \( \tau \)

Assumption: No additional degrees of freedom

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

Method 1: density in phase space

Energy:

\[ \varepsilon = \frac{p_x^2 + p_y^2 + p_z^2}{2M} \]

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

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

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

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

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

For \( N \) particles, the volume density between \( \bar{p} \) and \( \bar{p} + d\bar{p} = \frac{N}{V} \frac{1}{n_Q} \exp\left(-\frac{\varepsilon}{\tau}\right) \frac{d^3p}{h^3} \]

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

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 \( \hbar \) factor!

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

Individual States of probability $p_s$

\[ \varepsilon \rightarrow D(\varepsilon) d\varepsilon \rightarrow \varepsilon + d\varepsilon \]

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

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

$D(\varepsilon) d\varepsilon$ 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)

\[ p_s(\varepsilon) = \frac{1}{Z} \exp\left(-\frac{\varepsilon}{\tau}\right) \quad \text{and using} \quad p = \sqrt{2M\varepsilon} \quad d^3p = p^2 dp \cos \theta d\varphi = p^2 dp d\Omega \]

\[ D(\varepsilon)d\varepsilon = \int V d^3x \int \text{angles} \frac{p^2 d\varphi}{h^3} d\Omega = \frac{V4\pi}{h^3} p^2 \frac{dp}{d\varepsilon} d\varepsilon = \frac{V4\pi}{h^3} \frac{1}{2} (2M)^{3/2} \sqrt{\varepsilon} d\varepsilon = \frac{V}{4\pi^2} \left(\frac{2M}{h}\right)^{3/2} \sqrt{\varepsilon} d\varepsilon \]
In class

Partition Function for 2 systems

How do I get the partition function for 2 systems in weak interactions?
How do I get the partition function for 2 systems in weak interactions?

- A: the sum of partition functions
- B: the product of partition functions
- C: the sum of the logs
- D: the product of partition functions divided by 2!
Partition Function for 2 systems

How do I get the partition function for 2 systems in weak interactions?

B: the product of partition functions if the systems are distinguishable

D: $\approx$ the product of partition functions divided by 2! if the systems are indistinguishable
Weak interaction limit

2 sub systems in weak interaction:

\[ \Psi_{1+2}(n_1, n_2) = \Psi_1(n_1)\Psi_2(n_2) \text{ with } n_1, n_2 \text{ still meaningful} \]

\[ \Rightarrow \text{ Partition functions multiply for distinguishable systems} \]

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

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

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

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

![Graph of M vs. B](image1.png)

![Graph of M vs. $\tau$](image2.png)
**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 $Z(1)Z(2) = \sum_{s_1} e^{-\frac{E_{s_1}}{\tau}} \sum_{s_2} e^{-\frac{E_{s_2}}{\tau}}$ 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

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

If we have a large number of possible states, most of the terms are of the form $N!a_i a_j \ldots a_k$ 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)
Why is this approximate

Why is the division of the product by \( N! \) approximate?
Why is this approximate?

Why is the division of the product by $N!$ approximate?

A: It is actually rigorous
B: This is a large $N$ approximation
C: This is a low concentration approximation: no two systems in the same states
D: The systems are interacting, therefore the product is approximate
In class

Why is this approximate?

Why is the division of the product by N! approximate?

C: This is a low concentration approximation: the probability of having two systems in the same state is negligible.

For 2 systems \( Z \approx \frac{1}{2!} \sum s_1 \sum s_2 \exp\left(-\frac{\varepsilon_{s_1} + \varepsilon_{s_2}}{\tau}\right) \Rightarrow Z(1+2) = \frac{Z(1)Z(2)}{2!} \)

OK for 2 different states 1,2 is indistinguishable from 2,1

\[
\exp\left(-\frac{\varepsilon_1 + \varepsilon_2}{\tau}\right) + \exp\left(-\frac{\varepsilon_2 + \varepsilon_1}{\tau}\right) \text{ has to be divided by 2!}
\]

But the terms where we have the same state \( \exp\left(-\frac{\varepsilon_1 + \varepsilon_1}{\tau}\right) \)

should not be divided by 2
Ideal Gas

\( N \) atoms

Indistinguishable

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

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

\[
\log Z_N = N \log \left( \frac{n_Q}{n} \right) + N \quad \text{with } n = \frac{N}{V} = \text{concentration}
\]

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

Interpretation: \( n_Q \) as quantum concentration

de Broglie wave length

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

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

Energy

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

Equipartition of energy \(1/2 \tau\) per degree of freedom

Free energy

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

Free energy

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

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

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

\[ \mu = \frac{\partial F}{\partial N} = \frac{\partial \left( -\tau N \log \left( \frac{n_Q V}{N} \right) - \tau N \right)}{\partial N} = \tau \log \left( \frac{n}{n_Q} \right) \]
In class

Why use $F$?

Why not use $\mu = -\tau \frac{\partial \sigma}{\partial N}$?

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

Why not use?

\[ \mu = -\tau \frac{\partial \sigma}{\partial N} \]

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

Don't we get

\[ -\tau \log \frac{n_Q}{n} - \tau \left( -\frac{N}{N} + \frac{5}{2} \right) = \tau \left( \log \frac{n}{n_Q} - \frac{3}{2} \right) \]

Why is it different?

A: we cannot use \( \mu = -\tau \frac{\partial \sigma}{\partial N} \)

B: you can use it but with the proper independent variables being fixed

C: We are missing something
In class

Why use F

Why not use F?

\[ \mu = -\tau \frac{\partial \sigma}{\partial N} \]

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

\[ -\tau \frac{\partial \sigma}{\partial N} \bigg|_{\tau, V} = -\tau \log \frac{n_Q}{n} - \tau \left( -\frac{N}{N} + \frac{5}{2} \right) = \tau \left( \log \frac{n}{n_Q} - \frac{3}{2} \right) \]

Why is it different

\( \mu = -\tau \frac{\partial \sigma}{\partial N} \quad \text{B: you can use it but with the proper independent variables being fixed} \)

\[ -\tau \frac{\partial \sigma}{\partial N} \bigg|_{\tau, V} = -\tau \log \frac{n_Q}{n} - \tau \left( -\frac{N}{N} + \frac{5}{2} \right) = \tau \left( \log \frac{n}{n_Q} - \frac{3}{2} \right) \]

\[ \neq \mu = -\tau \frac{\partial \sigma}{\partial N} \bigg|_{U, V} = -\tau \frac{\partial}{\partial N} \left[ N \left( \log \left( \frac{M}{2 \pi \hbar^2} \right)^{3/2} \left( \frac{V}{N} \right) \right) \right] = -\tau \log \frac{n_Q}{n} - \tau \left( -\frac{N}{N} - \frac{3N}{2N} + \frac{5}{2} \right) \]

\[ = \tau \log \frac{n}{n_Q} \quad \text{v} \]

\[ \varepsilon \]
Barometric Equation: Three different ways

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

Thermodynamic equilibrium between slabs at various \( z \)

At constant temperature \( \mu_{\text{total}} = C \)

\[ \tau \log \frac{n(z)}{n_Q} = -\Phi(z) + C \iff n(z) = n_0 \exp \left( -\frac{mgz}{\tau} \right) \]

Single particle occupancy of levels at different altitude

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

Hydrodynamic equilibrium

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

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

Generalizes to case when the temperature is not constant.
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 \( \approx 10^{-2} \) eV

Rotation energy \( \epsilon_j = j(j+1)\epsilon_0 \) with multiplicity \( 2j+1 \)

\[
Z_{\text{int}} = \sum_j (2j+1) \exp \left( - \frac{j(j+1)\epsilon_0}{\tau} \right) = \int_{-1/2}^{1/2} (2j+1) \exp \left( - \frac{j(j+1)\epsilon_0}{\tau} \right) dj
\]

\[
= \frac{\tau}{\epsilon_0} \int_0^\infty \exp(-x) dx \quad \text{with} \quad x = \frac{j(j+1)\epsilon_0}{\tau} \approx \frac{(2j+1)\epsilon_0}{\tau} dj, x_0 = -\frac{\epsilon_0}{4\tau}
\]

\[ \Rightarrow Z_{\text{int}} = \frac{\tau}{\epsilon_0} \exp \left( \frac{\epsilon_0}{4\tau} \right) \quad \text{for} \ \tau \gg \epsilon_0 \quad \Rightarrow \quad \tau \gg \epsilon_0 \quad U = \frac{\tau^2 \partial \log Z}{\partial \tau} = \tau \quad C_{\text{rot}} = k_B
\]

For \( \tau < \epsilon_0 \), keep the first terms of the discrete sum

\[
\log Z_{\text{int}} \approx 3 \exp \left( -2 \frac{\epsilon_0}{\tau} \right) \quad U = \frac{\tau^2 \partial \log Z}{\partial \tau} \approx 6\epsilon_0 \exp \left( -2 \frac{\epsilon_0}{\tau} \right) \quad C_{\text{rot}} \approx 12k_B \left( \frac{\epsilon_0}{\tau} \right)^2 \exp \left( -2 \frac{\epsilon_0}{\tau} \right) \approx 0
\]

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

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

Spin in a magnetic field etc..
Evolution of the number of states of the Reservoir

Total system = Our system + reservoir
Configuration: 1 state $s$ of $S$
of energy $\varepsilon_s$ and # of particles $N_{is}$
+ energy of reservoir

Exchange of energy and particles

Question: How does the number of states of the reservoir change when we increase the energy of the system $S$? (the number of particles in system $S$ stay constant)

A: the number of states decreases
B: the number of states increases
C: the number of states stay constant
In class

Evolution of the number of states of the Reservoir

Total system = Our system + reservoir
Configuration: 1 state $s$ of $S$
of energy $\varepsilon_s$ and # of particles $N_{is}$
+ energy of reservoir

Exchange of energy and particles

**Question:** How does the number of states of the reservoir change when we increase the energy of the system $S$? (the number of particles in system $S$ stay constant)

**A:** the number of states decreases

$$g(R,U_0 - \varepsilon_s) = g(R,U_0) \exp\left(-\frac{\partial \sigma}{\partial U} \varepsilon_s\right) = g(R,U_0) \exp\left(-\frac{\varepsilon_s}{\tau}\right) \tau > 0$$
Evolution of the number of states of the Reservoir

Exchange of energy and particles

Question: How does the number of states of the reservoir change when we increase the number of particles in the system $S$? (the energy in system $S$ stay constant)

A: the number of states decreases
B: the number of states increases
C: it depends

Total system =Our system + reservoir
Configuration: 1 state $s$ of $S$
of energy $\varepsilon_s$ and # of particles $N_{is}$+
energy of reservoir
Evolution of the number of states of the Reservoir

Total system =Our system + reservoir
Configuration: 1 state s of S
of energy $\varepsilon_s$ and # of particles $N_{is}$
+ energy of reservoir

Exchange of energy and particles

Question: How does the number of states of the reservoir change when we increase the number of particles in the system $S$? (the energy in system $S$ stay constant)

C: it depends

$$g(R,U_0 - \varepsilon_s,N_0 - N_s) = g(R,U_0)\exp\left(-\frac{\partial \sigma_R}{\partial U} \varepsilon_s\right)\exp\left(-\frac{\partial \sigma_R}{\partial N} N_s\right) \equiv g(R,U_0)\exp\left(-\frac{\varepsilon_s}{\tau}\right)\exp\left(\frac{\mu N_s}{\tau}\right) \tau > 0$$

For an ideal gas $\mu = \tau \log\left(\frac{n}{n_Q}\right) < 0 \Rightarrow$ the number of states in reservoir decreases when $N_s$ increases

True also for Bose Einstein gas
But for Fermi Dirac $\mu = $Fermi level $> 0 \Rightarrow$ the number of states in reservoir increases when $N_s$ increases
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 \( \varepsilon \).

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

\[
= \left[ e^{5/2} \left( 1 + \frac{N}{N_p-N} \right)^{5/2} \gamma_p^{-N} \right]^{N_p-N} \left[ \left( \frac{M \frac{2U}{2\pi\hbar^2} \frac{3N_p}{3N_p}}{N_p} \right)^{3/2} \left( \frac{N_p}{V} \right)^{N_p-N} \right] \left[ \left( 1 - \frac{N\varepsilon}{U} \right)^{3/2} \gamma_p^{-N} \right]^{N_p-N} \]

\[
\Rightarrow \lim_{N \to \infty} \left[ e^{5/2} \frac{n_0}{n} \right]^{N} \exp\left(-N\log\frac{n_0}{n}\right) \exp\left(-\frac{N\varepsilon}{\tau}\right) \propto \exp\left(-\frac{N(\varepsilon - \mu)}{\tau}\right) \right] = b^N \equiv \exp\left(-N \log b\right)
\]
Gibbs factor

System in contact with thermal bath (reservoir)

Exchange of particles

\[ R, U_0 - \varepsilon \]

\[ S, \varepsilon \]

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

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

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

+ energy of reservoir

# States in configuration

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

At equilibrium

\[ \frac{\text{Pr ob}(\text{state } \varepsilon_1, N_{i1})}{\text{Pr ob}(\text{state } \varepsilon_2, N_{i2})} = \frac{g_R(U_o - \varepsilon_1, N_{oi} - N_{i1})}{g_R(U_o - \varepsilon_2, N_{oi} - N_{i2})} = \exp\left(-\frac{\partial \sigma}{\partial U}(\varepsilon_1 - \varepsilon_2) - \sum_i \frac{\partial \sigma}{\partial N_i}(N_{i1} - N_{i2})\right) \]

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

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

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

Notes:  

\( \mathcal{Z} = \text{grand partition function} \)
**Grand Partition Function**

**Definition**

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

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

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

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

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

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

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

This formalism is useful only if the \( N_{is} \) change.
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 $\varepsilon$

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

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

How is $\mu$ determined?

A: The density of $O_2$ in the blood
B: The vapor pressure in the atmosphere
C: Not enough information to say
How is $\mu$ determined?

A: The density of $O_2$ in the blood

<=$\text{dissolved gas is in equilibrium with absorption sites}$

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

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

Langmuir adsorption isotherm

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

**Comparison with 2 level system**

**Adsorption**

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

**2 level system: no \( \mu \)**

\[ Pr_{ob}(2) = \frac{\exp\left(-\frac{\varepsilon}{\tau}\right)}{1 + \exp\left(-\frac{\varepsilon}{\tau}\right)} = \frac{1}{1 + \exp\left(-\frac{\varepsilon}{\tau}\right)} \]
Adsorption dependences

**Adsorption**

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

\( \text{same form as Fermi-Dirac} \)

**Adsorption dependence on } \mu? \**

if } \mu \text{ increases (higher concentration or vapor pressure)

A: Fraction of occupied sites increases

B: Fraction of occupied sites decreases

C: Fraction is constant
Adsorption dependences

Adsorption

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

Adsorption dependence on \( \mu \)?

if \( \mu \) increases (higher concentration or vapor pressure)

A: Fraction of occupied sites increases

Denominator decreases

\( \rightarrow \) e.g., oxygen mask
Adsorption dependences

**Adsorption**

Fraction occupied: \( f = \frac{1}{\exp\left(\frac{\varepsilon - \mu}{\tau}\right) + 1} = \frac{p}{\tau n Q \exp\left(\frac{\varepsilon}{\tau}\right) + p} \)

**Adsorption dependence on \( \tau \)?**

If \( \tau \) increases (keeping pressure constant)

A: Fraction of occupied sites increases

B: Fraction of occupied sites decreases

C: It depends on the sign of \( \varepsilon - \mu \)
In class

Adsorption dependences

**Adsorption**

Fraction occupied: \( f = \frac{1}{\exp\left(\frac{\varepsilon - \mu}{\tau}\right) + 1} = \frac{p}{\tau n Q \exp\left(\frac{\varepsilon}{\tau}\right) + p} \)

**Adsorption dependence on \( \tau \)?**

- if \( \tau \) increases
- B: Fraction of occupied sites decreases

\(-\mu = \tau \log\left(\frac{n_0}{n}\right) > 0\)
\(\varepsilon < 0\) = binding energy  \(\exp\left(\frac{\varepsilon}{\tau}\right) < 1\)

Fraction occupied: \( f = \frac{1}{\exp\left(\frac{\varepsilon - \mu}{\tau}\right) + 1} = \frac{p}{\tau n Q \exp\left(\frac{\varepsilon}{\tau}\right) + p} \geq \frac{p}{\tau n Q + p} \)

(the larger the binding energy \(\varepsilon\), the bigger is the fraction of occupied site)

\(\tau \to \infty \quad f \to \frac{p}{\tau n Q + p} \approx \frac{n}{n_0}\) from above

At large \( \tau \), this is small! Most of the sites are emptied by the thermal fluctuation
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\textsuperscript{+} : no electron \rightarrow energy= 0
State 2=neutral 1 extra electron spin up \rightarrow energy =ε\textsubscript{d}
State 3= neutral 1 extra electron spin down \rightarrow energy =ε\textsubscript{d}

Fraction ionized \( f = \frac{1}{1 + \frac{2}{Z} \exp\left(-\frac{ε\textsubscript{d} - μ}{τ}\right)} \)

\( ε\textsubscript{d} = \text{energy of electron on donor site} \)
K\&K use ionization energy \( Ι = -ε\textsubscript{d} \)

Acceptor= tends to have 1 fewer electron (e.g. Al in Si)
State 1= ionized A\textsuperscript{-} : one electron completing the bond \rightarrow energy= ε\textsubscript{a}
State 2= 1 neutral: missing a bond electron spin up \rightarrow energy =0
State 3= 1 neutral: missing a bond electron spin down \rightarrow energy =0

Fraction ionized \( f = \frac{\exp\left(-\frac{ε\textsubscript{a} - μ}{τ}\right)}{\exp\left(-\frac{ε\textsubscript{a} - μ}{τ}\right) + \frac{2}{Z} \exp\left(-\frac{μ - ε\textsubscript{a}}{τ}\right)} = \frac{1}{1 + 2 \exp\left(-\frac{μ - ε\textsubscript{a}}{τ}\right)} \)

\( ε\textsubscript{a} = \text{energy of electron on acceptor site} \)

\( μ \) determined by electron concentration in semiconductor
\begin{align*}
&= \text{Fermi level}
\end{align*}
Grand Partition Function

Relation to thermodynamic functions

- Mean number of particles

\[ \langle N_i \rangle = \sum_s \sum_{N_{is}} N_{is} P_{s,N_{is}} = \sum_s \sum_{N_{is}} \frac{N_{is}}{3} \exp \left( \frac{\sum_i \mu_i N_{is} - \varepsilon(s,N_{is})}{\tau} \right) = \tau \frac{\partial \log 3}{\partial \mu_i} \bigg|_{\tau,V} \]

- Entropy

\[ \sigma = -\sum_s \sum_{N_{is}} p_{s,N_{is}} \log(p_{s,N_{is}}) = \log 3 - \sum_i \frac{\mu_i}{\tau} \langle N_{is} \rangle + \frac{\langle \varepsilon \rangle}{\tau} = \frac{\partial (\tau \log 3)}{\partial \tau} \bigg|_{V,\mu_i} \]

- Energy

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

- Free Energy

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

- Grand Potential \( \Omega \) defined as

\[ \Omega \equiv F - \sum_i \mu_i \langle N_i \rangle = -\tau \log 3 \]
In class

Note

Why $\sigma = \left. \frac{\partial (\tau \log Z)}{\partial \tau} \right|_{V, \mu_i}$ while $\Omega \equiv F - \sum_i \mu_i \langle N_i \rangle = -\tau \log Z$?
In class

Note

Why \( \sigma = \left. \frac{\partial (\tau \log 3)}{\partial \tau} \right|_{v, \mu_i} \) while \( \Omega \equiv F - \sum_i \mu_i \langle N_i \rangle = -\tau \log 3 \)?

A: Just an accident

B:

\[
F = \Omega + \sum_i \mu_i \langle N_i \rangle \quad \text{and} \quad \sigma = -\frac{\partial F}{\partial \tau} = -\frac{\partial \Omega}{\partial \tau} \quad \text{since} \quad \frac{\partial \sum_i \mu_i \langle N_i \rangle}{\partial \tau} = 0
\]

C: This is a consequence of the Thermodynamic identity
In class

Note

Why $\sigma = \frac{\partial (\tau \log Z)}{\partial \tau} \bigg|_{V, \mu_i}$ while $\Omega = F - \sum_i \mu_i \langle N_i \rangle = -\tau \log Z$?

C: This is a consequence of the Thermodynamic identity

$$dF = -\sigma d\tau - pdV + \sum_i \mu_i dN_i$$

$$\Omega = F - \sum_i \mu_i dN_i \Rightarrow d\Omega = \sigma d\tau - pdV - \sum_i N_i d\mu_i$$

$\Rightarrow \sigma = -\frac{\partial \Omega}{\partial \tau} \bigg|_{V, \mu_i}$

B: is terribly wrong $\frac{\partial \sum_i \mu_i \langle N_i \rangle}{\partial \tau} \bigg|_{V, \mu_i} \neq 0$

You are mixing independent variables

$$\sigma = -\frac{\partial F}{\partial \tau} \bigg|_{V, N_i} = -\frac{\partial \Omega}{\partial \tau} \bigg|_{V, \mu_i}$$

First expression is not useful because $N_i$ fluctuates
**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 $\approx N \times$ mean

$$U = \langle \varepsilon \rangle = \sum_s \varepsilon_s p_s = \sum_s \varepsilon_s \frac{e^{\frac{\varepsilon_s}{\tau}}}{Z}$$

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

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

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

$$U = \langle E \rangle = \frac{\tau^2 \partial \log Z}{\partial \mu}$$

Computation with partition function; By substitution we can see that

$$\sigma_E^2 = \langle E^2 \rangle - \langle E \rangle^2 = \frac{\tau^2 \partial U}{\partial \tau} = \tau^2 \frac{\partial^2 \log Z}{\partial \mu}$$

Similarly when there is exchange of particles

$$\langle N \rangle = \left| \frac{\partial \log Z}{\partial \mu} \right|_{\tau,V}$$

and

$$\sigma_N^2 = \langle N^2 \rangle - \langle N \rangle^2 = \frac{\partial \langle N \rangle}{\partial \mu}$$
**Examples**

**Fermi Dirac**

Fermions = particles with half integer spin

Pauli exclusion principle: each state contains at most one particle

For a state of energy $\varepsilon$

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

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

$$\sigma_N^2 = \frac{\partial \langle N \rangle}{\partial \mu} = \frac{\exp\left(\frac{\varepsilon - \mu}{\tau}\right)}{\left[\exp\left(\frac{\varepsilon - \mu}{\tau}\right) + 1\right]^2} = \langle N \rangle (1 - \langle N \rangle) \leq \langle N \rangle \quad \text{Less fluctuation than a Poisson distribution}$$
Bose Einstein

Bosons = particles with integer spin

For a state of energy $\varepsilon$

$$3 = \sum_N \exp \left( -\frac{[\varepsilon - \mu]N}{\tau} \right) = \frac{1}{1 - \exp \left( -\frac{\varepsilon - \mu}{\tau} \right)}$$

$$\langle N \rangle = \tau \frac{\partial \log 3}{\partial \mu} \bigg|_{r,v} = \frac{\exp \left( -\frac{\varepsilon - \mu}{\tau} \right)}{1 - \exp \left( -\frac{\varepsilon - \mu}{\tau} \right)} = \frac{1}{\exp \left( \frac{\varepsilon - \mu}{\tau} \right) - 1}$$

$$\sigma_N^2 = \frac{\tau \partial \langle N \rangle}{\partial \mu} = \frac{\exp \left( \frac{\varepsilon - \mu}{\tau} \right)}{\exp \left( \frac{\varepsilon - \mu}{\tau} \right) - 1}^2 = \langle N \rangle \left( 1 + \langle N \rangle \right) \leq \langle N \rangle \quad \text{More fluctuation than a Poisson distribution}$$
Does a system in thermal contact with a reservoir go to a state of minimum energy?
Does a system in thermal contact with a reservoir goes to a state of minimum energy?

A: Of course, this is a law of physics!
B: Yes, because this maximizes the number of states in the reservoir
C: No, because of the constant exchange of energy.
D: No, because of the Boltzmann factor
In class

Note

Does a system in thermal contact with a reservoir goes to a state of minimum energy?

C or D

C: No, because of the constant exchange of energy.
   The system is constantly kicked

D: No, because of the Boltzmann factor
   The Boltzmann factor does express this fact

A: “Of course, this is a law of physics!” is wrong because the system not only can emit energy (and go to minimum energy) but also can receive energy from the reservoir.

B: Yes, because this maximizes the number of states in the reservoir
   The state of $S$ of minimum energy is the most probable but other states are possible with smaller probabilities
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

\[ F_L(U_S) \equiv U_S - \tau_R \sigma_S(U_S) \]  

Landau Free Energy (constant volume)

\[ G_L(U_S,V_S) \equiv U_S - \tau_R \sigma_S(U_S,V_S) + p_R V_S \]  

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**

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

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

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

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

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

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

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

$$U_S = \frac{3}{2} N \tau_R$$

$\rho$, $U-U_S$, $S,U_S$
Exchange of Particles

If we exchange particles, what is minimized is

$$\Omega_L(U_S, N_S) = U_S - \tau_R \sigma_S(U_S, N_S) - \mu_R N_S$$

in a way similar to the previous slide

$$\sigma_{tot}(U_S, N_S) = \sigma_R(U - U_S, N - N_S) + \sigma_S(U_S, N_S)$$

$$\approx \sigma_R(U) - \frac{\partial \sigma_R}{\partial U} U_S - \frac{\partial \sigma_R}{\partial N} N_S + \sigma_S(U_S, N_S)$$

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

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

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

Note that this implies

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