

Statistical Mechanics  
from the context of the course  
PHY 410: Statistical Mechanics

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## 0.1 The SI System

In physics it's often important to have precisely defined units for the purposes of making very accurate measurements or simply having a coherent unit system. It's possible to derive all necessary units from five measurements of **length, mass, time, current, and temperature**. The standard SI units for these properties are listed below:

Type	Unit	Definition
Length	Meter( $m$ )	Length of distance light in a vacuum travels in $\frac{1}{299792458}$ seconds
Mass	Kilogram( $kg$ )	Defined by fixing the Planck's constant $h = 6.62607015 \times 10^{-34} kg \cdot m^2 s^{-1}$
Time	Second( $s$ )	Defined by fixing the ground-state hyperfine transition frequency of the caesium-133 atom, to be $9192631770 s^{-1}$
Current	Ampere( $A$ )	Defined by fixing the charge of an electron as $1.602176634 \times 10^{-19} A \cdot s$
Temperature	Kelvin( $K$ )	Defined by fixing the value of the Boltzmann constant $k$ to $1.380649 \times 10^{-23} kg \cdot m^2 s^{-2} K^{-1}$

Common prefixes are listed below:

Prefix	Symbol	Definition
mega	M	$10^6$
kilo	k	$10^3$
milli	m	$10^{-3}$
micro	$\mu$	$10^{-6}$
nano	$n$	$10^{-9}$
pico	$p$	$10^{-12}$
femto	$f$	$10^{-15}$

Additionally, the following are defined constants:

Symbol	Definition
$k_B$	$k_B = 1.380649 \times 10^{-23} m^2 s^{-2} K^{-1}$
$h$	$h = 6.62607015 \times 10^{-34} kg \cdot m^2 s^{-1}$
$\hbar$	$\hbar = \frac{h}{2\pi} \approx 1.0546 \times 10^{-34} kg \cdot m^2 s^{-1}$

## 0.2 Introduction

Statistical mechanics is the probabilistic study of extremely complex systems. It seeks to describe the equilibrium or averages behaviors of such systems. Very often in nature we deal with systems containing so many possible states that it would be impossible to completely describe and calculate the expected behavior. By focusing on large measurable properties of such systems and the average behavior of the microstates we can derive there behavior. With a combination of statistical arguments and microscopic knowledge, statistical mechanics predicts the macro equilibrium properties, which can be used to derive the laws of thermodynamics.

Thermodynamics is fundamentally connected with statistical mechanics and we will derive the laws of thermodynamics in the book. For reference here are the laws of thermodynamics.

**Law 0.2.1. The 0th Law of Thermodynamics** - Thermal equilibrium is transitive. If system  $A$  and  $B$  are in equilibrium and systems  $B$  and  $C$  are also in equilibrium, then systems  $A$  and  $C$  are in equilibrium.

**Law 0.2.2. The 1st Law of Thermodynamics** - Heat is a form of energy. Let  $\Delta E$  be the change in energy,  $W$  be the work done on the system, and  $Q$  the heat energy added to the system.

$$\Delta E = W + Q$$

**Law 0.2.3. The 2nd Law of Thermodynamics** - Total entropy always increases. Let  $\Delta S$  be the change in entropy and  $S_f$  and  $S_i$  be the final and initial entropy.

$$\Delta S = S_f - S_i > 0$$

$$\Delta S = \int_i^f \frac{1}{T} \partial Q = S_f - S_i$$

**Law 0.2.4. The 3rd Law of Thermodynamics** - Absolute Zero. Let  $S$  be entropy and  $T$  be temperature.

$$\lim_{T \rightarrow 0} S(T) = 0$$

We will seek to derive each of these laws in this book. Additionally, the logarithm function is used very often in statistical mechanics, we will used  $\log$  to refer to the natural logarithm (aka  $\log_e$ ).

## 0.3 Reference

A reference sheet is include on the next page. Click here (exam 1) or here (exam 2) for a pdf file



## PHY 410 - Reference Sheet

**Stirling's approximation** - for very large  $N$  the factorial can be very accurately approximated with the following

$$\log N! \approx N \log N - N$$

$$N! \approx \sqrt{2\pi N} N^N e^{-N}$$

**Fractional uncertainty** of  $\mathbb{X}$  is uncertainty of expected value per particle.

$$\frac{\Delta \mathbb{X}}{N} = \frac{\sqrt{\langle \mathbb{X}^2 \rangle - \langle \mathbb{X} \rangle^2}}{N}$$

**Boltzmann's constant**

$$k_B = 1.380649 \times 10^{-23} \text{ m}^2 \text{ s}^{-2} \text{ K}^{-1}$$

$$\text{Entropy } S = k_B \sigma, \quad \sigma_{TOT} = \sigma_1 + \sigma_2$$

$$\text{Temperature } T = \tau / k_B$$

## Microcanonical Ensemble

**Multiplicity function**

$$g = \# \text{ of microstates}, \quad \mathcal{P}(n) = \frac{1}{g}$$

**Expected value** of  $\mathbb{X}$  is the average across all microstates.

$$\langle \mathbb{X} \rangle = \sum_n \mathbb{X}(n) \mathcal{P}(n) = \frac{1}{g} \sum_n \mathbb{X}(n)$$

**Entropy** can be written in terms of the multiplicity function.

$$\sigma(N, T, U, V, P) \equiv \log[g(N, T, U, V, P)]$$

## Binary System

A **binary system** is a system of  $N$  particles where each particles has two possible states. Let  $N_\uparrow$  is the number of particle in the up state and  $N_\downarrow$  be the number of particles in the down state.

$$g(N, N_\uparrow) = \frac{N!}{N_\uparrow!(N - N_\uparrow)!}, \quad \sum_{N_\uparrow=0}^N g(N, N_\uparrow) = 2^N$$

The binary system can be rewritten in terms of the difference between up states and down states this is the **spin excess**.

$$2S = N_\uparrow - N_\downarrow$$

$$g(N, S) = \frac{N!}{(\frac{N}{2} + S)!(\frac{N}{2} - S)!}$$

$$\sum_{S=-\frac{N}{2}}^{\frac{N}{2}} g(N, N_\uparrow) = 2^N$$

Applying Stirling's approximation to the binary model, for large  $N$  the multiplicity function and fractional uncertainty are

$$g(N, S) \approx g(N, 0) e^{-2s^2/N}$$

$$g(N, S) \approx \sqrt{\frac{2}{\pi N}} 2^N e^{-2s^2/N}$$

$$\frac{\Delta S}{N} \approx \frac{1}{\sqrt{N}}$$

An example of a binary system is  $N$  spin 1/2 particles in an external **magnetic field**  $B$ . The total energy  $U$  and magnetization  $M$  of the system are

$$U = \sum_{i=1}^N -m\vec{i} \cdot \vec{B} = -(N_\uparrow - N_\downarrow)mB = -2SmB$$

$$M = 2Sm = -U/B$$

$$g(N, U) = \frac{N!}{(\frac{N}{2} - \frac{U}{2mB})!(\frac{N}{2} + \frac{U}{2mB})!}$$

$$\sigma(N, S) \approx -\left(\frac{N}{2} + S\right) \log\left(\frac{1}{2} + \frac{S}{N}\right) - \left(\frac{N}{2} - S\right) \log\left(\frac{1}{2} - \frac{S}{N}\right)$$

$$M = Nm \tanh(mB/\tau)$$

## Einstein Solid

An **einstein solid** is a system of  $N$  atoms where each atom is modeled as a harmonic oscillator the energy of the system is determined by the number of atoms  $n$  oscillating at frequency  $\omega$ .

$$U = n\hbar\omega$$

$$g(N, n) = \frac{(n + N - 1)!}{n!(N - 1)!}$$

$$g(N, n) \approx \left(\frac{n+N}{n}\right)^n \left(\frac{n+N}{N}\right)^N \frac{1}{\sqrt{2\pi n(n+N)/N}}$$

## Thermal Equilibrium

**Temperature**

$$\frac{1}{\tau} = \left(\frac{\partial \sigma}{\partial U}\right)_{N, V}$$

**Thermal Equilibrium**

$$\left(\frac{\partial \sigma_1}{\partial U_1}\right)_{N_1, V_1} = \left(\frac{\partial \sigma_2}{\partial U_2}\right)_{N_2, V_2}$$

$$\frac{1}{\tau_1} = \frac{1}{\tau_2}$$

**2nd law of thermo** - Change in entropy  $\geq 0$ .

**Sharpness of Equilibrium** For a two binary systems, the number of states in a configuration of deviation  $\delta$  from equilibrium is

$$g_1 g_2 = (g_1 g_2)_{max} e^{-\left(\frac{2\delta^2}{N_1} + \frac{2\delta^2}{N_2}\right)}$$

## Canonical Ensemble

**Partition Function** - partition by energy levels for a fixed temperature

$$z = \sum_n e^{-\varepsilon_n/\tau}, \quad \mathcal{P}(n) = \frac{1}{z} e^{-\varepsilon_n/\tau}$$

$$z = \sum_\alpha g(\varepsilon_\alpha) e^{-\varepsilon_\alpha/\tau}, \quad \text{for degeneracy } g(\varepsilon_\alpha)$$

**Expected Value** of  $\mathbb{X}$  is the average across all energies (Thermal Average).

$$\langle \mathbb{X} \rangle = \sum_n \mathbb{X}(n) \mathcal{P}(n) = \frac{1}{z} \sum_n \mathbb{X}(n) e^{-\varepsilon_n/\tau}$$

**Expected Energy** in the canonical ensemble is

$$U = \langle \varepsilon \rangle = \frac{1}{z} \sum_n \varepsilon_n e^{-\varepsilon_n/\tau}$$

$$U = \langle \varepsilon \rangle = \tau^2 \frac{1}{z} \frac{\partial z}{\partial \tau} = \tau^2 \frac{\partial}{\partial \tau} \log z$$

The total partition function and expected energy for  $N$  non-interacting particles is simply

$$z_N = z_1^N$$

$$U_N = \langle \varepsilon \rangle_N = N U_1 = N \langle \varepsilon \rangle_1$$

(this also applies for expected value of any  $\mathbb{X}$ )

## Thermodynamic Relations

**1st Law of Thermo**

$$dU = dQ + dW = \tau d\sigma - PdV$$

$$d\sigma = \frac{1}{\tau} dU + \frac{P}{\tau} dV$$

**Temperature**  $\tau = \left(\frac{\partial U}{\partial \sigma}\right)_V$

**Quasi-static Compression Equilibrium**

the equilibrium condition for quasi-static compression is

$$\left(\frac{\partial U_1}{\partial V_1}\right)_{\sigma_1} = \left(\frac{\partial U_2}{\partial V_2}\right)_{\sigma_2}$$

## Helmholtz Free Energy

$$F = U - \tau \sigma = U - ST = -\tau \log z$$

$$dF = -\sigma d\tau - PdV$$

**Entropy**  $\sigma = -\left(\frac{\partial F}{\partial \tau}\right)_V$ ,  $S = k_B \sigma$

**Pressure**

$$P = -\left(\frac{\partial U}{\partial V}\right)_\sigma = \tau \left(\frac{\partial \sigma}{\partial V}\right)_U = -\left(\frac{\partial F}{\partial V}\right)_\tau$$

**Energy**

$$U = -\tau^2 \frac{\partial}{\partial \tau} \left(\frac{F}{\tau}\right)$$

## Ideal Gas

**DeBroglie Thermal Wavelength** is the wavelength of the wave functions of matter at a given temperature.

$$\lambda_T = \sqrt{\frac{2\pi\hbar^2}{m\tau}}$$

**Concentration** of a system is the inverse of the volume

$$n = \frac{1}{V}$$

**Quantum Concentration** is the density of quantum state per particle. It is used to define when a system will behave classically ( $n \ll n_Q$ ) and when a system will be dominated by quantum effects ( $n \gg n_Q$ ).

$$n_Q = \frac{1}{\lambda_T^3}$$

**Single Particle Ideal Gas** is a system in the canonical ensemble consisting of a single particle in a box of side lengths  $L$ . The energy levels, partition function and average energy are

$$E_{n_x, n_y, n_z} = \frac{\hbar^2}{2m} \left(\frac{\pi}{L}\right)^2 (n_x^2 + n_y^2 + n_z^2)$$

$$z_1 = \frac{V}{\lambda_T^3}$$

$$U_1 = \frac{3}{2} \tau$$

$$\sigma_1 = \log\left(\frac{V}{\lambda_T^3}\right) + \frac{3}{2}$$

**Gibbs Resolution** states that for systems in the classical regime the partition function for an ideal gas with  $N$  particles is

$$z_N = \frac{1}{N!} (z_1)^N$$

$$U_N = \frac{3}{2} N \tau$$

$$\sigma_N = N \left[ \log\left(\frac{V}{N \lambda_T^3}\right) + \frac{5}{2} \right]$$

**N-Particle Ideal Gas** - by applying Gibbs resolution and properties of expected values we can find the classical ideal gas results

$$PV = N \tau$$

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

$$\sigma = N \left[ \log\left(\frac{V}{N \lambda_T^3}\right) + \frac{5}{2} \right]$$

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## PHY 410 - Reference Sheet

**Boltzmann's constant**  
 $k_B = 1.380649 \times 10^{-23} \text{ m}^2 \text{ s}^{-2} \text{ K}^{-1}$   
**Entropy**  $S = k_B \sigma$   
**Temperature**  $T = \tau / k_B$

## Canonical Ensemble

**Partition Function** - partition by energy levels for a fixed temperature

$$z = \sum_n e^{-\varepsilon_n / \tau}, \quad \mathcal{P}(n) = \frac{1}{z} e^{-\varepsilon_n / \tau}$$

**Expected Value** of  $\mathbb{X}$  is the average across all energies (Thermal Average).

$$\langle \mathbb{X} \rangle = \sum_n \mathbb{X}(n) \mathcal{P}(n) = \frac{1}{z} \sum_n \mathbb{X}(n) e^{-\varepsilon_n / \tau}$$

**Expected Energy** in the canonical ensemble is

$$U = \langle \varepsilon \rangle = \frac{1}{z} \sum_n \varepsilon_n e^{-\varepsilon_n / \tau}$$

$$U = \langle \varepsilon \rangle = \tau^2 \frac{1}{z} \frac{\partial z}{\partial \tau} = \tau^2 \frac{\partial}{\partial \tau} \log z$$

The total partition function and expected value for  $N$  non-interacting particles is simply

$$z_N = z_1^N$$

$$\langle \mathbb{X} \rangle_N = N \langle \mathbb{X} \rangle_1 \Rightarrow U_N = N U_1$$

**Helmholtz Free Energy**

$$F = U - \tau \sigma = U - S T = -\tau \log z$$

$$dF = -\sigma d\tau - P dV$$

**Entropy**  $\sigma = -\left(\frac{\partial F}{\partial \tau}\right)_V$ ,  $S = k_B \sigma$   
**Pressure**

$$P = -\left(\frac{\partial U}{\partial V}\right)_\sigma = \tau \left(\frac{\partial \sigma}{\partial V}\right)_U = -\left(\frac{\partial F}{\partial V}\right)_\tau$$

**Energy**  $U = -\tau^2 \frac{\partial}{\partial \tau} \left(\frac{F}{\tau}\right)$

## Thermal Radiation

**Single Frequency Photon Gas** is a system in the canonical ensemble that considers photons of a specific frequency  $\omega$ .

$$\varepsilon_s = s \hbar \omega, \quad s = 0, 1, 2, 3, \dots$$

$$z = \sum_{s=0}^{\infty} e^{-s \hbar \omega / \tau} = \frac{1}{1 - e^{-\hbar \omega / \tau}}$$

$$\mathcal{P}(s) = \frac{e^{-s \hbar \omega / \tau}}{z}$$

$$\langle s \rangle = \frac{1}{z} \sum_{s=0}^{\infty} s e^{-s \hbar \omega / \tau} = \frac{1}{e^{\hbar \omega / \tau} - 1}$$

**Photon Gas** is an expansion of the single frequency photon gas that considers all the possible cavity modes. The modes are 2 fold degenerate for the 2 independent polarizations.

$$\omega_n = \frac{c\pi}{L} \sqrt{n_x^2 + n_y^2 + n_z^2} = \frac{c\pi n}{L}$$

$$U = \langle \varepsilon \rangle = 2 \sum_n \frac{\hbar \omega_n}{e^{\hbar \omega_n / \tau} - 1} = \frac{\pi^2 V}{15(\hbar c)^3} \tau^4$$

**Stefan-Boltzmann Law**

$$\frac{U}{V} = \frac{\hbar}{\pi^2 c^3} \int_0^{\infty} \frac{\omega^3}{e^{\hbar \omega / \tau} - 1} d\omega = \frac{\pi^2}{15(\hbar c)^3} \tau^4$$

**Spectral Density Function**

$$\frac{\partial U}{\partial \omega} \frac{U}{V} = \frac{\hbar}{\pi^2 c^3} \frac{\omega^3}{e^{\hbar \omega / \tau} - 1}$$

**Flux Density** ( $\sigma_B = \text{Stefan-Boltzmann constant}$ )

$$J_\mu = \frac{1}{4} \frac{cU}{V} = \sigma_B \tau^4 = \frac{\pi^2}{60(\hbar c)^3} \tau^4$$

## Phonons in a Solid (Debye Model)

Phonons in a solid is a system in the canonical ensemble that is very similar to thermal radiation except there is 3 fold degeneracy from 3 polarizations of phonons and an upper cutoff frequency  $\omega_D$  due to the separation distance between atoms.

$$\omega_n = \frac{\pi c_S}{L} \sqrt{n_x^2 + n_y^2 + n_z^2} = \frac{\pi c_S}{L} n$$

**Debye cutoff frequency**

$$\omega_D = c_S \left( \frac{6\pi^2 N}{V} \right)^{1/3}, \quad \omega_D = \frac{\pi c_S}{L} n_D$$

## Grand Canonical Ensemble

**Chemical Potential**

$$\mu = \left( \frac{\partial F}{\partial N} \right)_{\tau, V}$$

$$\mu = \tau \log \left( \frac{N \lambda_T^3}{V} \right) = \tau \log \left( \frac{n}{n_Q} \right)$$

$$\mu = \left( \frac{\partial U}{\partial N} \right)_{\sigma, V} = -\tau \left( \frac{\partial \sigma}{\partial N} \right)_{U, V}$$

**Grand Partition Function** - partition by energy levels for a fixed temperature and all possible values of  $N$

$$z_\varepsilon = \sum_N \sum_{n(N)} e^{-(\varepsilon_n^N - \mu N) / \tau}$$

$$\mathcal{P}(N, \varepsilon_n) = \frac{1}{z_\varepsilon} e^{-(\varepsilon_n^N - \mu N) / \tau}$$

**Fugacity**

$$\lambda = e^{\mu / \tau}$$

$$z_\varepsilon = \sum_N \lambda^N \sum_{s(N)} e^{-\varepsilon_s^N / \tau} = \sum_N \lambda^N z_N$$

**Expected Value** of  $\mathbb{X}$  is the average across all energies (Diffusive Average).

$$\langle \mathbb{X} \rangle = \frac{1}{z_\varepsilon} \sum_N \sum_s \mathbb{X}(N, s) e^{-(\varepsilon_s^N - \mu N) / \tau}$$

**Expected Number of Particles** in the grand canonical ensemble is

$$N = \langle N \rangle = \tau \frac{\partial}{\partial \mu} \log z_\varepsilon = \lambda \frac{\partial}{\partial \lambda} \log z_\varepsilon$$

**Expected Energy** in the grand canonical ensemble is

$$U = \langle \varepsilon \rangle = \frac{1}{z_\varepsilon} \sum_N \sum_{n(N)} \varepsilon_n^N e^{-(\varepsilon_n^N - \mu N) / \tau}$$

$$U = \langle \varepsilon \rangle = \tau^2 \left( \frac{\partial}{\partial \tau} \log z_\varepsilon \right)_\lambda$$

**Concentration and DeBroglie Wavelength**

$$n = \frac{N}{V}, \quad n_Q = \frac{1}{\lambda_T^3}, \quad \lambda_T = \sqrt{\frac{2\pi \hbar^2}{m\tau}}$$

## Grand Potential

$$\Omega = U - \sigma \tau - \mu N$$

$$\Omega = -\tau \log z_\varepsilon$$

$$\sigma = \left( \frac{-\partial \Omega}{\partial \tau} \right)_{V, \mu}, \quad P = \left( \frac{-\partial \Omega}{\partial V} \right)_{\tau, \mu}, \quad N = \left( \frac{-\partial \Omega}{\partial \mu} \right)_{\tau, V}$$

## System of Non-interacting Particles

The grand partition function for a system with  $M$  energy states where  $n_\alpha$  is the number of particles occupying a state is

$$z_\varepsilon = \prod_{\alpha=1}^M z_\alpha, \quad z_\alpha = \sum_{n_\alpha} e^{-n_\alpha (\varepsilon_\alpha - \mu) / \tau}$$

$$U = \sum_{\alpha=1}^M \varepsilon_\alpha f(\varepsilon_\alpha), \quad N = \sum_{\alpha=1}^M f(\varepsilon_\alpha)$$

## Fermions

$$n_\alpha = 0, 1$$

$$z_\alpha = 1 + e^{-(\varepsilon_\alpha - \mu) / \tau} = 1 + \lambda e^{-\varepsilon_\alpha / \tau}$$

**Fermi-Dirac Distribution** is the expected number of a particles in a particular energy  $\varepsilon_\alpha$ .

$$\langle n_\alpha \rangle = f(\varepsilon_\alpha) = \frac{1}{e^{(\varepsilon_\alpha - \mu) / \tau} + 1} = \frac{1}{\lambda^{-1} e^{\varepsilon_\alpha / \tau} + 1}$$

**For  $\tau \rightarrow 0$ :**  $f(\varepsilon_\alpha) = \theta(\varepsilon_\alpha - \mu)$

**Bosons (Bosons)**

$$n_\alpha = 0, 1, 2, 3, \dots$$

$$z_\alpha = \frac{1}{1 - e^{-(\varepsilon_\alpha - \mu) / \tau}} = \frac{1}{1 - \lambda e^{-\varepsilon_\alpha / \tau}}$$

**Boson Distribution** is the expected number of a particles in a particular energy  $\varepsilon_\alpha$ .

$$\langle n_\alpha \rangle = f(\varepsilon_\alpha) = \frac{1}{e^{(\varepsilon_\alpha - \mu) / \tau} - 1} = \frac{1}{\lambda^{-1} e^{\varepsilon_\alpha / \tau} - 1}$$

## Ideal Gas

Both fermions and bosons behave identically at the classical limit  $\varepsilon_\alpha - \mu \gg \tau$ .

$$\langle n_\alpha \rangle = f(\varepsilon_\alpha) = e^{-(\varepsilon_\alpha - \mu) / \tau}$$

$$z_\varepsilon = \sum_N \lambda^N z_N = \sum_N \lambda^N \frac{1}{N!} z_1^N = e^{\lambda z_1}$$

$$\lambda = \frac{n}{n_Q}, \quad PV = N\tau, \quad U = \frac{3}{2} N\tau, \quad \mu = \tau \log \frac{n}{n_Q}$$

$$\sigma = N \left[ \log \frac{n_Q}{n} + \frac{5}{2} \right], \quad F = N\tau \left[ \log \frac{n}{n_Q} - 1 \right]$$

**Heat Capacity** measures the change in heat energy per unit temperature

$$C_P > C_V, \quad C_V = \left( \frac{\partial U}{\partial T} \right)_V = \tau \left( \frac{\partial \sigma}{\partial T} \right)_V$$

$$C_P = \left( \frac{\partial U}{\partial T} \right)_P + P \left( \frac{\partial V}{\partial T} \right)_P = \tau \left( \frac{\partial \sigma}{\partial T} \right)_P$$

**Monoatmc gas**  $C_V = \frac{3}{2} N k_B$ ,  $C_P = \frac{5}{2} N k_B$

**Isothermal Expansion**  $\sigma_f - \sigma_i = N \log \frac{V_f}{V_i}$

$$Q = N\tau \log \frac{V_f}{V_i}$$

**Isoentropic Expansion**  $\frac{\tau_f}{\tau_i} = \left( \frac{V_i}{V_f} \right)^{2/3}$

## Internal Excitations

Expansion of the ideal gas to take into account the additional energy states from internal excitations.

$$z_{int} = \sum_\alpha e^{-\varepsilon_\alpha / \tau}, \quad z_\varepsilon = 1 + \lambda z_{int} e^{-\varepsilon_n / \tau}$$

**Internal Excitation Corrections**

$$\lambda = \frac{n}{n_Q z_{int}}, \quad \mu = \tau \left( \log \frac{n}{n_Q} - \log z_{int} \right)$$

$$F = N\tau \left[ \log \frac{n}{n_Q} - 1 \right] - N\tau \log z_{int}$$

$$\sigma = N \left[ \log \frac{n}{n_Q} + \frac{5}{2} \right] - \left( \frac{\partial F_{int}}{\partial \tau} \right)_V$$

## DOG (bork)



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# Chapter 1

## Microcanonical Ensemble

Throughout this book we will refer to microscopic and macroscopic systems. Using Quantum mechanics one can predict the behavior of a small number of particles or similar small systems with high levels of symmetry. However, as the number of particles increases, Schrödinger's becomes practically impossible to solve. However the microscopic quantum states of a system determine many measurable macroscopic properties, such as temperature, energy, volume or pressure. Towards making predictions about these macroscopic properties it is useful to count the number of possible microstates for a given macrostate.

**Definition 1.0.1.** The **microcanonical ensemble** is the system of calculations where the total energy, particle number, and volume are fixed.

### 1.1 Multiplicity Functions

**Definition 1.1.1.** A **Multiplicity function** is the number of microstates that produce a given macrostate denoted

$$g(N, T, U, V, P) = \# \text{ of microstates that fit the given macrostate}$$

**Assumption 1.1.2. Boltzmann's Assumption** - All accessible microstates are equally probable. Let  $P(n)$  be the probability that a system is in microstate  $n$ .

$$\mathcal{P}(n) = \frac{1}{g(N, T, U, V, P)}$$

**Definition 1.1.3.** The **entropy** of a system is defined as the natural log of the multiplicity function.

$$\sigma(N, T, U, V, P) \equiv \log[g(N, T, U, V, P)]$$

**Definition 1.1.4.** The **expected value** of a property  $\mathbb{X}$  of a system is determined by the average of that value across all possible microstates.

$$\langle \mathbb{X} \rangle = \sum_n \mathbb{X}(n) \mathcal{P}(n) = \frac{1}{g} \sum_n \mathbb{X}(n)$$

**Definition 1.1.5.** The **fractional uncertainty** of a property  $\mathbb{X}$  is defined in terms of the expected value.

$$\frac{\Delta \mathbb{X}}{N} = \frac{\sqrt{\langle \mathbb{X}^2 \rangle - \langle \mathbb{X} \rangle^2}}{N}$$

## 1.2 Binary System

**Definition 1.2.1.** A **binary system** is a system of  $N$  particles where each particles has two possible states. Let  $N_\uparrow$  is the number of particle in the up state and  $N_\downarrow$  be the number of particles in the down state.

$$g(N, N_\uparrow) = \frac{N!}{N_\uparrow!(N - N_\uparrow)!}, \quad \sum_{N_\uparrow=0}^N g(N, N_\uparrow) = 2^N$$

**Corollary 1.2.2.** The binary system can be rewritten in terms of the **difference between up states and down states**.

$$2S = N_\uparrow - N_\downarrow$$

$$g(N, S) = \frac{N!}{(\frac{N}{2} + S)!(\frac{N}{2} - S)!}, \quad \sum_{S=-\frac{N}{2}}^{S=\frac{N}{2}} g(N, N_\uparrow) = 2^N$$

**Theorem 1.2.3. Stirling's Approximation** - for very large  $N$  the factorial can be very accurately approximated with the following

$$\begin{aligned} \log N! &\approx N \log N - N \\ N! &\approx \sqrt{2\pi N} N^N e^{-N} \end{aligned}$$

**Proposition 1.2.4.** Applying Stirling's approximation to the binary model, for large  $N$  the multiplicity function and fractional uncertainty are

$$\begin{aligned} g(N, S) &\approx g(N, 0) e^{-2s^2/N} \\ g(N, S) &\approx \sqrt{\frac{2}{\pi N}} 2^N e^{-2s^2/N} \\ \frac{\Delta S}{N} &\approx \frac{1}{\sqrt{N}} \end{aligned}$$

*Example.* Consider a system of  $N$  spin 1/2 particles in an external magnetic field  $B$ . The total energy  $U$  and magnetization  $M$  of the system are

$$\begin{aligned} U &= \sum_{i=1}^N -\vec{m}_i \cdot \vec{B} = -(N_\uparrow - N_\downarrow)mB = -2SmB \\ M &= 2Sm = -U/B \\ g(N, U) &= \frac{N!}{(\frac{N}{2} - \frac{U}{2mB})!(\frac{N}{2} + \frac{U}{2mB})!} \\ \sigma(N, S) &\approx -\left(\frac{N}{2} + S\right) \log\left(\frac{1}{2} + \frac{S}{N}\right) - \left(\frac{N}{2} - S\right) \log\left(\frac{1}{2} - \frac{S}{N}\right) \\ M &= Nm \tanh(mB/\tau) \end{aligned}$$

**Definition 1.2.5.** An **einstein solid** is a system of  $N$  atoms where each atom is modeled as a harmonic oscillator the total energy of the system is determined by the number of atoms  $n$  oscillating at frequency  $\omega$ .

$$\begin{aligned} U &= n\hbar\omega \\ g(N, n) &= \frac{(n + N - 1)!}{n!(N - 1)!} \\ g(N, n) &\approx \frac{\left(\frac{n+N}{n}\right)^n \left(\frac{n+N}{N}\right)^N}{\sqrt{2\pi n(n + N)/N}} \end{aligned}$$

### 1.3 Thermal Equilibrium

Since the uncertainty of our system is extremely small for large  $N$ , the most probable state as determined by Boltzmann's assumption will determine the macrostate of the system.

**Definition 1.3.1.** The **equilibrium** state two systems is the most probable macrostate of the shared system.

$$g_{TOT}(N, V, U) = \sum_{U'_1} g_1(N_1, V_1, U'_1) g_2(N_2, V_2, U - U'_1)$$

$$\mathcal{P}(U'_1) = \frac{g_1(N_1, V_1, U'_1) g_2(N_2, V_2, U - U'_1)}{g_{TOT}(N, V, U)}$$

*Example.* Consider two isolated binary systems

$$g_1(4, 2) \text{ and } g_2(6, 0)$$

The initial condition of the two states are  $N_1 = 4, S_1 = 2$  and  $N_2 = 6, S_2 = 0$ . Now, allowing contact between the two systems the equilibrium state is the most probable state that conserves energy. To find this we need to maximize the total multiplicity function

$$g(N_1 + N_2, S'_1, S'_2) = g_1(N_1, S'_1) g_2(N_2, S'_2)$$

For this simple system the max is found when  $S'_1 = 1$  and  $S'_2 = 1$ .

**Definition 1.3.2.** **Thermal equilibrium** is reached when the energy derivative of the total multiplicity function is zero.

$$\left( \frac{\partial \sigma_1}{\partial U_1} \right)_{N_1, V_1} = \left( \frac{\partial \sigma_2}{\partial U_2} \right)_{N_2, V_2}$$

**Definition 1.3.3.** The **temperature** of a system is defined with the derivative of entropy  $\sigma$  in terms of energy  $U$ . Kelvin temperature  $T$  is directly proportional to the fundamental temperature via the Boltzmann constant  $k_B$ .

$$\frac{1}{\tau} = \left( \frac{\partial \sigma}{\partial U} \right)_{N, V}$$

$$\tau = k_B T$$



## Chapter 2

# The Canonical Ensemble

Up until this point we've been working with closed systems where the total amount of energy is fixed. In the real world it is often very difficult to thermally isolate a system. It is much easier to operate at a fixed temperature and a fixed number of particles. We separate each of these cases into ensembles.

**Definition 2.0.1.** The **canonical ensemble** is the system of calculations where the temperature and particle number are fixed.

### 2.1 Partition Function

**Definition 2.1.1.** The **partition function** determines how we calculate probability. For a fixed temperature we partition by energy levels. The probability of a particular energy  $\varepsilon_n$  is given by

$$\mathcal{P}(\varepsilon_n) = \frac{1}{z} e^{-\varepsilon_n/\tau}$$
$$z = \sum_n e^{-\varepsilon_n/\tau}$$

**Corollary 2.1.2.** For systems with degeneracy  $g(\varepsilon_\alpha)$  for each distinct energy level  $\varepsilon_\alpha$ , the partition function can be rewritten.

$$z = \sum_\alpha g(\varepsilon_\alpha) e^{-\varepsilon_\alpha/\tau}$$

**Definition 2.1.3.** The **thermal average** of  $\mathbb{X}$  is the average across all energies).

$$\langle \mathbb{X} \rangle = \sum_n \mathbb{X}(n) \mathcal{P}(n) = \frac{1}{z} \sum_n \mathbb{X}(n) e^{-\varepsilon_n/\tau}$$

**Definition 2.1.4.** The **expected energy** in the canonical ensemble is

$$U = \langle \varepsilon \rangle = \frac{1}{z} \sum_n \varepsilon_n e^{-\varepsilon_n/\tau}$$
$$U = \langle \varepsilon \rangle = \tau^2 \frac{1}{z} \frac{\partial z}{\partial \tau} = \tau^2 \frac{\partial}{\partial \tau} \log z$$

*Example.* One and many simple harmonic oscillators at temperature  $\tau$ . Starting with a system of just one harmonic oscillator we find

$$\varepsilon_n = \left(n + \frac{1}{2}\right) \hbar \omega$$
$$z_1 = \sum_n e^{-(n+\frac{1}{2})\frac{\hbar\omega}{\tau}} = \frac{e^{-\hbar\omega/2\tau}}{1 - e^{-\hbar\omega/\tau}}$$
$$U_1 = \langle \varepsilon \rangle = \frac{\hbar\omega}{2} + \frac{\hbar\omega e^{-\hbar\omega/\tau}}{1 - e^{-\hbar\omega/\tau}} = \frac{\hbar\omega}{2} + \frac{\hbar\omega}{e^{-\hbar\omega/\tau} - 1}$$

Now, consider a system of  $N$  simple harmonic oscillators at temperature  $\tau$ .

$$z_N = \sum_{n_1, n_2, \dots, n_N} e^{-\frac{1}{\tau}(\varepsilon_{n_1} + \varepsilon_{n_2} + \dots + \varepsilon_{n_N})} = z_1^N$$
$$U_N = \langle \varepsilon \rangle = \tau^2 \frac{\partial}{\partial \tau} \log z_N = N \tau^2 \frac{\partial}{\partial \tau} \log z = \frac{N \hbar \omega}{2} + \frac{N \hbar \omega}{e^{-\hbar\omega/\tau} - 1} = N U_1$$

## 2.2 Reversible Processes

**Definition 2.2.1.** A **quasi-static process** is an idealization where parameters are changed so slowly that the system is indefinitely close to thermal and mechanical equilibrium during the process.

**Definition 2.2.2.** A **reversible process** is a quasi-static process where the system retraces its steps if you reverse the changes in the parameters.

**Definition 2.2.3.** The **pressure** of a system is defined as the negative derivative of energy with respect to volume.

$$P_n = - \left( \frac{\partial \varepsilon_n}{\partial V} \right)_\sigma$$

$$P = \langle -\frac{\partial \varepsilon_n}{\partial V} \rangle = \sum_n -\frac{\partial \varepsilon_n}{\partial V} e^{-\varepsilon_n/\tau}$$

**Proposition 2.2.4.** For quasi-static compression the pressure is simply the derivative of energy with respect to volume.

$$P = -\frac{\partial}{\partial V} \frac{1}{z} \sum_n \varepsilon_n e^{-\varepsilon_n/\tau} = - \left( \frac{\partial U}{\partial V} \right)_\sigma = \tau \left( \frac{\partial \sigma}{\partial V} \right)_U$$

## 2.3 Helmholtz Free Energy

**Definition 2.3.1.** The **Helmholtz Free Energy**  $F$  of a system is defined in terms of the energy  $U$  the entropy  $\sigma$ ,  $S$  and the temperature  $\tau$ ,  $T$ .

$$F = U - \sigma\tau = U - ST$$

**Proposition 2.3.2.** Equilibrium in the canonical ensemble is achieved when the Helmholtz free energy  $F$  is minimized

$$\partial F = 0, \quad \Delta F \leq 0$$

**Proposition 2.3.3.** The entropy, pressure, and expected energy of a system in the canonical ensemble can be written in terms of the Helmholtz free energy.

$$\sigma = - \left( \frac{\partial F}{\partial \tau} \right)_V, \quad P = - \left( \frac{\partial F}{\partial V} \right)_\tau, \quad U = -\tau^2 \frac{\partial}{\partial \tau} \left( \frac{F}{\tau} \right)$$

**Proposition 2.3.4.** The Helmholtz free energy is determined by the temperature  $\tau$  and partition function  $z$ .

$$F = -\tau \log z$$

$$z = e^{-F/\tau}$$

**Definition 2.3.5.** **Maxwell relations** are relations that are derive from the following form

$$df = A dx + B dy$$

$$\frac{\partial}{\partial y} \frac{\partial f}{\partial x} = \frac{\partial}{\partial x} \frac{\partial f}{\partial y}$$

**Proposition 2.3.6.** Using Maxwell relations we can derive the following

$$dU = \tau d\sigma - P dV$$

$$\left( \frac{\partial \sigma}{\partial V} \right)_\tau = \left( \frac{\partial P}{\partial \tau} \right)_V$$

$$\left( \frac{\partial P}{\partial \sigma} \right)_V = - \left( \frac{\partial \tau}{\partial V} \right)_\sigma$$

## 2.4 Ideal Gas

**Definition 2.4.1.** The **concentration** of a system is the inverse of the volume

$$n = \frac{1}{V}$$

**Definition 2.4.2.** The **quantum concentration** is the density of quantum state per particle. It is used to define when a system will behave classically (when  $n \ll n_Q$ ) and when a system will be dominated by quantum effects (when  $n \gg n_Q$ ).

$$n_Q = \frac{1}{\lambda_T^3}$$

**Definition 2.4.3.** The **DeBroglie thermal wavelength** is the wavelength of the wave functions of matter at a given temperature.

$$\lambda_T = \sqrt{\frac{2\pi\hbar^2}{m\tau}}$$

**Definition 2.4.4.** **Single particle ideal gas** is a system in the canonical ensemble consisting of a single particle in a box of side lengths  $L$ . The energy levels, partition function and average energy are

$$E_{n_x, n_y, n_z} = \frac{\hbar^2}{2m} \left(\frac{\pi}{L}\right)^2 (n_x^2 + n_y^2 + n_z^2)$$

$$z_1 = \sum_{n_x, n_y, n_z} e^{\frac{-E_{n_x, n_y, n_z}}{\tau}} = \left(L\sqrt{\frac{m\tau}{\hbar^2 2\pi}}\right)^3 = \frac{V}{\lambda_T^3} = \frac{n_Q}{n} = \frac{V}{\lambda_T^3}$$

$$U_1 = \frac{3}{2}\tau$$

$$\sigma_1 = \log\left(\frac{V}{\lambda_T^3}\right) + \frac{3}{2}$$

**Proposition 2.4.5.** **Gibbs resolution** states that for systems in the classical regime the partition function for an ideal gas with  $N$  particles is

$$z_N = \frac{1}{N!} (z_1)^N$$

$$U_N = \frac{3}{2} N\tau$$

$$\sigma_N = N \left[ \log\left(\frac{V}{N\lambda_T^3} + \frac{5}{2}\right) \right]$$

**Law 2.4.6.** **Ideal gas law** states that the pressure and volume are related to temperature and particle number

$$PV = N\tau$$

$$PV = Nk_B T$$

## 2.5 Ideal Diatomic Gas

**Definition 2.5.1.** **Single particle diatomic gas** is a system in the canonical ensemble consisting of a single particle in a box with vibration and rotational excitation. The energy levels, partition function and average energy are

$$E_{\vec{p}, n, \ell} = \frac{\rho^2}{2m} + \left(n + \frac{1}{2}\right)\hbar\omega_{vib} + \frac{\hbar^2}{2I}\ell(\ell+1)$$

$$z_1 = \sum_{\vec{p}, n, \ell} (2\ell+1) e^{-[E_{KE} + E_{Vib} + E_{Rot}]/\tau} = \frac{V}{\lambda_T^3} + \sum_n e^{-(n+\frac{1}{2})\hbar\omega/\tau} + \sum_\ell (2\ell+1) e^{\frac{\hbar^2 \ell(\ell+1)}{2I}/\tau}$$

$$U_1 = \frac{3}{2}N\tau + \delta U_{Vib} + \delta U_{Rot}$$

$$U_1 = -\tau \log\left(\frac{V}{\lambda_T^3}\right) + \delta F_{Vib} + \delta F_{Rot}$$

## 2.6 Thermal Radiation

**Definition 2.6.1. Photons** - For light at a given frequency  $\omega = 2\pi f$ , the energy levels are

$$\varepsilon_s = s\hbar\omega, \quad s = 0, 1, 2, 3, \dots$$

These energy levels are very similar to the simple harmonic oscillator  $E_n = (n + \frac{1}{2})\hbar\omega$ . So we can use the example from earlier to derive the partition function.

$$\begin{aligned} z &= \sum_{s=0}^{\infty} e^{-s\hbar\omega/\tau} = \frac{1}{1 - e^{-\hbar\omega/\tau}} \\ \mathcal{P}(s) &= \frac{e^{-s\hbar\omega/\tau}}{z} \\ \langle s \rangle &= \frac{1}{z} \sum_{s=0}^{\infty} s e^{-s\hbar\omega/\tau} = \frac{1}{e^{\hbar\omega/\tau} - 1} \\ \langle \epsilon \rangle &= \frac{\hbar\omega}{e^{\hbar\omega/\tau} - 1} \end{aligned}$$

**Definition 2.6.2.** A **thermal cavity** or **photon gas** is a system in the microcanonical ensemble that describes the extension of a single photon to account for all the possible frequencies in a chamber. Consider a cubic thermal cavity of side length  $L$ . There are two possible polarizations for each of the three directions in the cube.

$$\begin{aligned} \omega_N &= \frac{c\pi}{L} \sqrt{n_x^2 + n_y^2 + n_z^2} = \frac{c\pi}{L} \vec{n} \\ U = \langle \epsilon \rangle &= 2 \sum_n \frac{\hbar\omega_n}{e^{\hbar\omega_n/\tau} - 1} = \frac{\hbar V}{\pi^2 c^3} \int_0^{\infty} \frac{\omega^3}{e^{\hbar\omega/\tau} - 1} d\omega = \frac{\pi^2 V}{15(\hbar c)^3} \tau^4 \\ \sigma &= \frac{4\pi^2 V}{45(\hbar c)^3} \tau^3 \\ P &= \frac{1}{3} \frac{U}{V} \end{aligned}$$

**Definition 2.6.3.** The **Stefan Boltzmann law** states that the energy per unit volume of a thermal cavity at temperature  $\tau$  is

$$\frac{U}{V} = \frac{\hbar}{\pi^2 c^3} \int_0^{\infty} \frac{\omega^3}{e^{\hbar\omega/\tau} - 1} d\omega = \frac{\pi^2}{15(\hbar c)^3} \tau^4$$

In classical physics, this energy is defined with an infinite sum that doesn't converge. Therefore, the energy is infinite. This is known as the ultraviolet catastrophe.

**Definition 2.6.4.** The **spectral density function** of a thermal cavity is the expected energy per unit volume per unit frequency at a given frequency  $\omega$

$$\frac{\partial}{\partial \omega} \frac{U}{V} = \frac{\hbar}{\pi^2 c^3} \frac{\omega^3}{e^{\hbar\omega/\tau} - 1}$$

**Proposition 2.6.5.** The maximal spectral frequency of a radiating object at fixed temperature is found when

$$\begin{aligned} 3 - 3e^{-\hbar\omega_{\max}/\tau} &= \frac{\hbar\omega_{\max}}{\tau} \\ \tau &\approx \frac{\hbar\omega_{\max}}{2.82} \end{aligned}$$

**Proposition 2.6.6.** From the 1st law of thermodynamics, entropy of thermal radiation is

$$\sigma(\tau, V) = \frac{4\pi^2 V}{45(\hbar c)^3} \tau^3$$

**Proposition 2.6.7.** Furthermore the pressure of thermal radiation is

$$P = \frac{1}{3} \frac{U}{V} = \frac{\pi^2}{45(\hbar c)^3} \tau^4$$

**Proposition 2.6.8.** The **Heat capacity** of the photon gas is

$$C_v = \left( \frac{\partial U}{\partial T} \right)_{N,V} = \frac{4V\pi^2}{15(\hbar c)^3} \tau^3$$

Towards deriving some useful insights from this model we will consider a small hole in the side of the cavity. This represents a perfect black body. From the energy density and some geometry we can show that

$$J_\mu = \frac{U}{V} \frac{U}{V} = \frac{\pi^2}{60(\hbar c)^3} \tau^4$$

**Definition 2.6.9.** The **Flux density** is the energy emitted per unit time per unit area from a black body. It is related to the temperature by the Stefan Boltzmann constant denoted  $\sigma_B$ .

$$J_\mu = \frac{\pi^2}{60(\hbar c)^3} \tau^4 = \frac{\pi^2 k_B^4}{60(\hbar c)^3} T^4 = \sigma_B T^4$$

**Definition 2.6.10.** The **emissivity** of an object is a factor between 0 and 1 that determines how much radiation is emitted or reflected. An emissivity of 1 is a perfect black body and 0 is a perfect mirror.

$$J_{real} = e \cdot J_\mu$$

## 2.7 Phonons in a Solid

The excitations that we have been considering for light can also be generalized to describe vibrations and sound waves in solid materials.

**Definition 2.7.1.** A **phonon** is a vibrational excitation in a solid. We will consider  $N$  atoms in a lattice. The energy levels are

$$\varepsilon_s = s\hbar\omega, \quad s = 0, 1, 2, 3, \dots$$

The energy levels can be used identically to the photon case to derive a partition function and the average number of phonons at a given frequency and temperature.

$$z = \sum_{s=0}^{\infty} e^{-s\hbar\omega/\tau} = \frac{1}{1 - e^{-\hbar\omega/\tau}}$$

$$\mathcal{P}(s) = \frac{e^{-s\hbar\omega/\tau}}{z}$$

$$\langle s \rangle = \frac{1}{z} \sum_{s=0}^{\infty} s e^{-s\hbar\omega/\tau} = \frac{1}{e^{\hbar\omega/\tau} - 1}$$

$$\langle \epsilon \rangle = \frac{\hbar\omega}{e^{\hbar\omega/\tau} - 1}$$

**Definition 2.7.2.** A **phonon gas** is a system in the microcanonical ensemble that describes the extension of a single phonon to account for the distribution of frequencies in a solid. The system uses a model of the distribution of frequencies to make predictions

### 2.7.3 Einstein Model

The einstein model assumes that all the oscillations in a solid are at the same frequency  $\omega$ .

**Proposition 2.7.4.** With the Einstein model the average energy and heat capacity are

$$U = \frac{3N\hbar\omega}{e^{\hbar\omega/\tau} - 1}$$

$$C_V = k_B \left( \frac{\partial U}{\partial \tau} \right)_{V,N} = 3N \left( \frac{\hbar\omega}{\tau} \right)^2 \frac{e^{\hbar\omega/\tau}}{(e^{\hbar\omega/\tau} - 1)^2}$$

### 2.7.5 Debye Model

The Debye model takes into account the possible standing waves in the solid. For a given speed of sound  $c_s$  the Debye frequencies are

$$\omega_{n_x, n_y, n_z} = \frac{\pi c_s}{L} \sqrt{n_x^2 + n_y^2 + n_z^2} = \frac{\pi c_s}{L} \vec{n}$$

For phonons, there are three modes of polarization. Unlike the photon case where the frequency continues to infinity, there is a maximum oscillation frequency that the solid can support. This frequency is determined by the spacing of the lattice and the speed of sound.

**Definition 2.7.6.** The **Debye cutoff frequency**  $\omega_D$  is the maximum oscillation frequency that the solid with  $N$  atoms, volume  $V$ , and speed of sound  $c_s$  can support.

$$\omega_D = c_s \left( \frac{6\pi^2 N}{V} \right)^{1/3} = \frac{\pi c_s}{L} n_D$$

**Proposition 2.7.7.** The average energy of the phonon gas is determined by the following integral.

$$U = \frac{3V}{2\pi^2} \frac{\hbar}{c_s^3} \int_0^{\omega_D} \frac{\omega^3 d\omega}{e^{\hbar\omega/\tau} - 1}$$

In the dimensionless variable  $x = \hbar\omega/\tau$  the energy is

$$U = \frac{3}{2} \frac{V\tau^4}{\pi^2 (\hbar c_s)^3} \int_0^{x_D} \frac{x^3 dx}{e^x - 1} \quad x_D = \frac{\hbar\omega_D}{\tau}$$

**Proposition 2.7.8.** In the low  $\tau$  limit ( $\tau \ll \hbar\omega$ ), this integral can be evaluated exactly. The average energy and heat capacity at this limit are

$$U \approx \frac{3c_s^3 \tau^4 \pi^4}{5\omega_D^3 \pi^2 (\hbar c_s)^3}$$

$$C_V = \left( \frac{\partial U}{\partial T} \right)_{N,V} = \frac{12\pi^4 N k_B}{5(\omega_D \hbar c_s)^3} T^3$$

## Chapter 3

# Grand Canonical Ensemble

Up until this point we've been working with a system where the total number of particles is fixed. In the Grand Canonical Ensemble the particle number of the system is allowed to exchange with the environment.

**Definition 3.0.1.** The **chemical potential** can be used to determine if a system is in diffusive equilibrium.

$$\mu = \left( \frac{\partial F}{\partial N} \right)_{\tau, V}$$

*Remark.* When several species of particles are present each species has its own  $\mu$ . In the grand canonical ensemble, each of these chemical potentials is fixed by the environment.

**Proposition 3.0.2.** Using thermodynamic relations we can derive the following alternate equations for the chemical potential

$$\mu = \tau \log \left( \frac{N \lambda_T^3}{V} \right) = \tau \log \left( \frac{n}{n_Q} \right) = -\tau \left( \frac{\partial \sigma}{\partial N} \right)_{U, V} = \left( \frac{\partial U}{\partial N} \right)_{\sigma, V}$$

### 3.1 Grand Partition Function

**Definition 3.1.1.** The **grand partition function** determines the probability of a given energy. For a fixed temperature and chemical potential, the probability of a particular energy  $\varepsilon_n$  is given by

$$\mathcal{P}(N, \varepsilon_n) = \frac{1}{\mathcal{Z}_\lambda} e^{-(\varepsilon_n^N - \mu N)/\tau}$$
$$\mathcal{Z}_\lambda = \sum_N \lambda^N \sum_{s(N)} e^{-\varepsilon_s^N/\tau} = \sum_N \lambda^N \mathcal{Z}_N$$

**Definition 3.1.2.** The **fugacity** is the effective partial pressure of a real gas denoted  $\lambda$  that can be used to write the grand partition function.

$$\lambda = e^{\mu/\tau}$$
$$\mathcal{Z}_\lambda = \sum_N \lambda^N \sum_{s(N)} e^{-\varepsilon_s^N/\tau}$$

**Definition 3.1.3.** The **diffusive average** of  $\mathbb{X}$  is the average across all energies

$$\langle \mathbb{X} \rangle = \frac{1}{\mathcal{Z}_\lambda} \sum_N \sum_s \mathbb{X}(N, s) e^{-(\varepsilon_s^N - \mu N)/\tau}$$

**Proposition 3.1.4.** The average number of particles can be found from the grand partition function.

$$N = \langle N \rangle = \tau \frac{\partial}{\partial \mu} \log \mathcal{Z}_\lambda = \lambda \frac{\partial}{\partial \lambda} \log \mathcal{Z}_\lambda$$

**Proposition 3.1.5.** the expected energy can be found from the grand partition function.

$$U = \langle \varepsilon \rangle = \frac{1}{\mathcal{Z}_\lambda} \sum_N \sum_{n(N)} \varepsilon_n^N e^{-(\varepsilon_n^N - \mu N)/\tau} = \tau^2 \left( \frac{\partial}{\partial \tau} \log \mathcal{Z}_\lambda \right)_\lambda$$

## 3.2 Grand Potential

**Definition 3.2.1.** The **grand potential** is a measurement similar to the Helmholtz free energy to determine if a system is in equilibrium.

$$\Omega = U - \sigma\tau - \mu N$$

**Proposition 3.2.2.** Equilibrium in the grand canonical ensemble is achieved when the grand potential is minimized.

$$\partial\Omega = 0, \quad \Delta\Omega \leq 0$$

**Proposition 3.2.3.** The grand potential can be determined from the grand partition function

$$\Omega = -\tau \log z_i$$

**Proposition 3.2.4.** The entropy, pressure, and average particle number can be written in terms of the grand potential.

$$\sigma = - \left( \frac{\partial\Omega}{\partial\tau} \right)_{V,\mu}, \quad P = - \left( \frac{\partial\Omega}{\partial V} \right)_{\tau,\mu}, \quad N = - \left( \frac{\partial\Omega}{\partial\mu} \right)_{\tau,V}$$

## 3.3 Fermions and Bosons

**Proposition 3.3.1.** The grand partition function for a system with  $M$  energy states where  $n_\alpha$  is the number of particles occupying a state is

$$z_i = \prod_{\alpha=1}^M z_{\alpha}, \quad z_{\alpha} = \sum_{n_{\alpha}} e^{-n_{\alpha}(\varepsilon_{\alpha}-\mu)/\tau}$$

For such a system with energy states and particles to occupy those states there are two possibilities.

**Definition 3.3.2.** A **fermion** is a particle with half integer spin. Each energy state can only be occupied by 1 particle.

$$n_{\alpha} = 0, 1$$

$$z_{\alpha} = 1 + e^{-(\varepsilon_{\alpha}-\mu)/\tau} = 1 + \lambda e^{-\varepsilon_{\alpha}/\tau}$$

**Definition 3.3.3.** The **fermi-dirac distribution** is the expected number of a particles in a particular energy state  $\varepsilon_{\alpha}$  for fermions.

$$\langle n_{\alpha} \rangle = f(\varepsilon_{\alpha}) = \frac{1}{e^{(\varepsilon_{\alpha}-\mu)/\tau} + 1} = \frac{1}{\lambda^{-1}e^{\varepsilon_{\alpha}/\tau} + 1}$$

**Proposition 3.3.4.** For the zero temperature limit  $\tau \rightarrow 0$ , the fermi dirac distribution is a step function centered at the chemical potential.

$$f(\varepsilon_{\alpha}) = \theta(\varepsilon_{\alpha} - \mu)$$

**Definition 3.3.5.** A **boson** is a particle with integer spin. Each energy state can be occupied by many particles.

$$n_{\alpha} = 0, 1, 2, 3, \dots$$

$$z_{\alpha} = \frac{1}{1 - e^{-(\varepsilon_{\alpha}-\mu)/\tau}} = \frac{1}{1 - \lambda e^{-\varepsilon_{\alpha}/\tau}}$$

**Definition 3.3.6.** The **bose-einstein distribution** is the expected number of particles in a particular energy state  $\varepsilon_{\alpha}$  for bosons.

$$\langle n_{\alpha} \rangle = f(\varepsilon_{\alpha}) = \frac{1}{e^{(\varepsilon_{\alpha}-\mu)/\tau} - 1} = \frac{1}{\lambda^{-1}e^{\varepsilon_{\alpha}/\tau} - 1}$$

**Proposition 3.3.7.** the expected energy and expected number of particles for both fermions and bosons can be found from the expected occupancy function

$$U = \sum_{\alpha=1}^M \varepsilon_{\alpha} f(\varepsilon_{\alpha}), \quad N = \sum_{\alpha=1}^M f(\varepsilon_{\alpha})$$

**Proposition 3.3.8.** Both fermions and bosons behave identically at the classical limit  $\varepsilon_{\alpha} - \mu \gg \tau$ . This agrees with Gibb resolution from the canonical ideal gas.

$$\langle n_{\alpha} \rangle = e^{-(\varepsilon_{\alpha}-\mu)/\tau}$$

$$\log z_i = \lambda z_1$$



### 3.4 Grand Ideal Gas

We now have the definitions to consider the ideal gas in the grand canonical ensemble.

**Proposition 3.4.1.** For an ideal gas in the grand canonical ensemble the following equations hold

$$\begin{aligned}\langle n_\alpha \rangle &= f(\varepsilon_\alpha) = e^{-(\varepsilon_\alpha - \mu)/\tau} \\ z_i &= \sum_N \lambda^N z_N = \sum_N \lambda^N \frac{1}{N!} z_1^N = e^{\lambda z_1} \\ \lambda &= \frac{n}{n_Q}, \quad PV = N\tau, \quad U = \frac{3}{2}N\tau, \quad \mu = \tau \log \frac{n}{n_Q} \\ \sigma &= N \left[ \log \frac{n_Q}{n} + \frac{5}{2} \right], \quad F = N\tau \left[ \log \frac{n}{n_Q} - 1 \right]\end{aligned}$$

**Definition 3.4.2.** The **heat capacity** of a material is the change in heat energy with respect to temperature when fixing volume or pressure.

$$\begin{aligned}(\partial Q)_V &= C_V \partial T \\ (\partial Q)_P &= C_P \partial T\end{aligned}$$

**Proposition 3.4.3.** For an ideal gas the heat capacities with fixed volume and pressure are

$$\begin{aligned}C_V &= \left( \frac{\partial U}{\partial T} \right)_V = \tau \left( \frac{\partial \sigma}{\partial T} \right)_V \\ C_P &= \left( \frac{\partial U}{\partial T} \right)_P + P \left( \frac{\partial V}{\partial T} \right)_P = \tau \left( \frac{\partial \sigma}{\partial T} \right)_P \\ C_P &> C_V\end{aligned}$$

**Proposition 3.4.4.** For a monoatomic ideal gas the heat capacities are

$$\begin{aligned}C_V &= \frac{3}{2} N k_B \\ C_P &= \frac{5}{2} N k_B\end{aligned}$$

*Example. Isothermal Expansion* - Consider the case of the slow isothermal expansion of an ideal gas. In this case, no energy is exchanged with the environment. Work is done on the piston and heat energy flows into the system.

$$\Delta U = 0, \quad U = \frac{3}{2} N \tau, \quad Q > 0$$

$$\sigma_f - \sigma_i = N \log \frac{V_f}{V_i}$$

$$Q = N \tau \log \frac{V_f}{V_i}$$

*Example. Isoentropic Expansion* - Consider the case of the slow isoentropic expansion of an ideal gas. In this case, the entropy of the gas is fixed.

$$\Delta \sigma = 0, \quad Q = 0$$

$$\frac{\tau_f}{\tau_i} = \left( \frac{V_i}{V_f} \right)^{\frac{2}{3}}$$

### 3.4.5 Ideal Gas with Internal Degrees of Freedom

We can extend this model of an ideal gas to consider the effect of internal degrees of freedom.

**Definition 3.4.6.** An **ideal gas with internal degrees of freedom** is an expansion of the ideal gas to take into account the additional energy states from internal excitations.

$$z_{int} = \sum_{\alpha} e^{-\varepsilon_{\alpha}/\tau}$$

$$z_i = 1 + \lambda z_{int} e^{-\varepsilon_n/\tau}$$

**Proposition 3.4.7.** For an ideal gas with internal degrees of freedom the following equations hold

$$\lambda = \frac{n}{n_Q z_{int}}$$

$$\mu = \tau \left( \log \frac{n}{n_Q} - \log z_{int} \right)$$

$$F = N\tau \left[ \log \frac{n}{n_Q} - 1 \right] - N\tau \log z_{int}$$

$$\sigma = N \left[ \log \frac{n}{n_Q} + \frac{5}{2} \right] - \left( \frac{\partial F_{int}}{\partial \tau} \right)_V$$

## 3.5 Fermi Gas

At low temperature the fermi-dirac distribution acts like a step function at  $\mu$ . This critical energy emerges at quantum concentrations.

**Definition 3.5.1.** The **fermi energy** denoted  $\varepsilon_F$  is the highest occupied energy level at  $\tau = 0$

$$\varepsilon_F = \mu(\tau = 0)$$

**Definition 3.5.2.** The **ground state energy** is the expected energy at zero temperature.

$$U_0 = U(\tau = 0)$$

**Definition 3.5.3.** The **density of states** denoted  $D(\varepsilon)$  is number of available states per unit energy.

$$\langle \mathbb{X} \rangle = \sum_{\mathbf{n}} f(\varepsilon_{\mathbf{n}}) \mathbb{X}_{\mathbf{n}} = \int_0^{\infty} D(\varepsilon) f(\varepsilon) \mathbb{X}(\varepsilon) d\varepsilon$$

**Proposition 3.5.4.** The expected energy and expected number of particles can be written in terms of the density of states

$$U = \int_0^{\infty} \varepsilon D(\varepsilon) f(\varepsilon) d\varepsilon$$

$$N = \int_0^{\infty} D(\varepsilon) f(\varepsilon) d\varepsilon$$

At  $\tau = 0$ , the integrals can be reduced

$$U(\tau = 0) = \int_0^{\varepsilon_F} \varepsilon D(\varepsilon) d\varepsilon$$

$$N(\tau = 0) = \int_0^{\varepsilon_F} D(\varepsilon) d\varepsilon$$

Consider a fermi gas of  $N$  spin- $\frac{1}{2}$  particles in a 3d box at  $\tau = 0$ .

$$\varepsilon_n = \frac{\hbar^2 \pi^2}{2mL^2} n^2, \quad n = 1, 2, 3, 4, \dots$$

$$\varepsilon_F = \frac{\hbar^2 \pi^2}{2mL^2} n_F^2$$

**Proposition 3.5.5.** By counting the  $N$  particles in the gas we can find the fermi energy.

$$N = \pi \frac{n_F^3}{3} \quad \Rightarrow \quad n_f = \left( \frac{3N}{\pi} \right)^{1/3}$$

$$\varepsilon_F = \frac{\hbar^2}{2m} \left( \frac{3\pi^2 N}{V} \right)^{2/3} = \frac{\hbar^2}{2m} (3\pi^2 n)^{2/3} = \tau_F$$

**Proposition 3.5.6.** Using this temperature, we can find the ground state energy and pressure

$$U_0 = \frac{3}{5} N \varepsilon_F$$

$$P_0 = \frac{2}{3} \frac{U_0}{V}$$

**Proposition 3.5.7.** For a fermi gas the density of states is

$$D(\varepsilon) = \frac{V}{2\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} \varepsilon^{1/2}$$

**Proposition 3.5.8.** For small  $\tau \ll \varepsilon_F$ , the chemical potential and expected energy are

$$\mu(\tau \ll \varepsilon_F) = \varepsilon_F \left( 1 - \frac{\pi^2}{12} \frac{\tau^2}{\varepsilon_F^2} \right)$$

$$U(\tau \ll \varepsilon_F) = U_0 + \frac{\pi^2}{4} \left( \frac{\tau}{\varepsilon_F} \right)^2 N \varepsilon_F$$

## 3.6 Bose-Einstein Condensate

Bosons at quantum concentration form a Bose-Einstein condensate. At  $\tau = 0$  all the particles can fit in the ground state. For low temperature the expected number of particles in the ground state approaches  $N$ .

**Definition 3.6.1.** The **Condensate** denoted  $N_0(\tau)$  is the number of particles in the ground state.

$$N_0(\tau) = \langle n_{\varepsilon_0} \rangle = f(\varepsilon_0, \tau) = \frac{1}{e^{(\varepsilon_0 - \mu)/\tau} - 1}$$

$$\lim_{\tau \rightarrow 0} N_0(\tau) = N$$

**Definition 3.6.2.** The **Normal Phase** denoted  $N_e(\tau)$  is the number of particles not in the ground state.

$$N_e(\tau) = N - N_0(t)$$

**Proposition 3.6.3.** At low  $\tau \approx 0$ , the following limits apply

$$N_0(\tau) \approx \frac{\tau}{\varepsilon_0 - \mu}$$

$$\mu \approx \varepsilon_0 - \frac{\tau}{N}$$

Consider a boson gas of  $N$  spin- $\frac{1}{2}$  particles in a 3d box at  $\tau \approx 0$ .

$$\varepsilon_n = \frac{\hbar^2 \pi^2}{2mL^2} (n_x^2 + n_y^2 + n_z^2) = \frac{\hbar^2 \pi^2}{2mL^2} \vec{n}^2, \quad \vec{n} = 1, 2, 3, 4, \dots$$

**Proposition 3.6.4.** For a 3d boson gas the condensate is

$$N_0 = \frac{1}{e^{-\mu/\tau} - 1} = \frac{1}{\lambda^{-1} - 1}$$

**Proposition 3.6.5.** For a 3d boson gas the normal phase is

$$N_e = \frac{V}{4\pi^2} \left( \frac{2m}{\hbar} \right)^{3/2} \int_0^\infty \frac{\varepsilon^{1/2} d\varepsilon}{\lambda^{-1} e^{\varepsilon/\tau} - 1}$$

**Proposition 3.6.6.** For a 3d boson gas the maximum possible value of the normal phase at a fixed temperature  $\tau$  is

$$(N_e)_{max} = \frac{V}{4\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} \tau^{3/2} \int_0^\infty \frac{x^{1/2} dx}{e^x - 1} \approx 2.612 \left( \frac{m\tau}{2\pi\hbar^2} \right)^{3/2} = 2.612 n_Q V$$

$$\frac{N_e(\tau)}{N} = 2.612 \frac{n_Q}{n}$$

**Definition 3.6.7.** The **critical concentration** denoted  $n_E$  is the smallest concentration with bose-einstein condensation.

$$n_E = \frac{(N_e)_{max}}{V} = 2.612 n_Q$$

**Definition 3.6.8.** The **critical temperature** denoted  $\tau_E$  is the maximum temperature with bose-einstein condensation.

$$\tau_E = \frac{2\pi\hbar^2}{m} \left( \frac{n}{2.612} \right)^{3/2}$$

**Proposition 3.6.9.** For  $\tau < \tau_E$  the normal phase and condensate are approximately

$$N_e(\tau) = N \left( \frac{\tau}{\tau_E} \right)^{3/2}$$

$$N_0(\tau) = N \left( 1 - \left( \frac{\tau}{\tau_E} \right)^{3/2} \right)$$

# Chapter 4

## Thermodynamics

Now we have developed the necessary technology to derive the laws of thermodynamics. This chapter will focus on applications of thermodynamics and the macroscopic implications of the relations we have derived.

**Law 4.0.1.** The **First Law of Thermodynamics** states that the total energy of a closed system is conserved.

$$dU = dQ + dW, \quad \text{for reversible process:} \quad dU = \tau d\sigma + dW$$

**Definition 4.0.2.** **Work** is energy transfer that does not change entropy.

**Definition 4.0.3.** **Heat** is energy transfer that does change entropy.

### 4.1 Heat Engines and Refrigerators

**Definition 4.1.1.** A **heat engine** is any devices that converts transfer of heat into work,  $Q_H/\sigma_H$  denotes the heat/entropy transferred from the hot reservoir,  $Q_C/\sigma_C$  denotes the heat/entropy transferred to the cold reservoir, and  $W$  denotes the work extracted.

**Proposition 4.1.2.** For a reversible heat engine, the entropy transferred from/to the hot/cold reservoir is determined by

$$\sigma_H = \frac{Q_H}{\tau_H}, \quad \sigma_C = \frac{Q_C}{\tau_C}$$

**Definition 4.1.3.** The **engine efficiency** denoted  $\eta$  is the amount of work extracted per unit of heat transferred.

$$\eta = \frac{W}{Q_H} = \frac{Q_H - Q_C}{Q_H}$$

**Definition 4.1.4.** The **carnot efficiency** denoted  $\eta_c$  is the engine efficiency of a reversible heat engine.

$$\eta_c = 1 - \frac{Q_C}{Q_H} = 1 - \frac{\tau_C}{\tau_H}$$

**Proposition 4.1.5.** The engine efficiency of an engine is less than or equal to the carnot efficiency.

$$\eta \leq \eta_c \quad \left( \frac{Q_C}{Q_H} \right)_{real} \geq \left( \frac{Q_C}{Q_H} \right)_{rev}$$

**Proposition 4.1.6.** The carnot engine cycle can be constructed by four segments of expansion and compression.

1. Isothermal expansion from  $\sigma_L$  to  $\sigma_H$ .
2. Isoentropic expansion from  $\tau_H$  to  $\tau_C$ .
3. Isothermal compression from  $\sigma_H$  to  $\sigma_L$ .
4. Isoentropic compression from  $\tau_C$  to  $\tau_H$ .

**Definition 4.1.7.** A **refrigerator** is any device that converts work into transfer of heat,  $Q_H/\sigma_H$  denotes the heat/entropy transferred to the hot reservoir,  $Q_C/\sigma_C$  denotes the heat/entropy transferred from the cold reservoir, and  $W$  denotes the work used.

**Proposition 4.1.8.** For a reversible refrigerator, the entropy transferred to/from the hot/cold reservoir is determined by

$$\sigma_H = \frac{Q_H}{\tau_H}, \quad \sigma_C = \frac{Q_C}{\tau_C}$$

**Definition 4.1.9.** The **coefficient of performance** denoted  $\gamma$  is the amount of heat transferred per unit of work used.

$$\gamma = \frac{Q_H}{W} = \frac{Q_C}{Q_H - Q_C}$$

**Definition 4.1.10.** The **carnot coefficient of performance** denoted  $\gamma_c$  is the coefficient of performance of a reversible refrigerator.

$$\gamma_c = \frac{1}{\frac{Q_H}{Q_C} - 1} = \frac{1}{\frac{\tau_H}{\tau_C} - 1} = \frac{\tau_C}{\tau_H - \tau_C}$$

**Proposition 4.1.11.** The coefficient of performance of a refrigerator is less than or equal to the carnot coefficient of performance.

$$\gamma \leq \gamma_c \quad \left( \frac{Q_H}{Q_C} \right)_{real} \geq \left( \frac{Q_H}{Q_C} \right)_{rev}$$

**Proposition 4.1.12.** An analogous carnot refrigerator cycle can be constructed by simply reversing the direction of the carnot engine cycle.

## 4.2 Gibbs free energy

The isothermal–isobaric ensemble describes systems with fixed temperature, pressure and particle number  $(\tau, P, N)$ . Such a system is common under atmospheric conditions and there is a concept analogous to the Helmholtz free energy for this case.

**Definition 4.2.1.** The **Gibbs free energy** denoted  $G$  is minimized at equilibrium for a system in the isothermal–isobaric ensemble.

$$G = U - \tau\sigma + PV$$

**Definition 4.2.2.** The **effective work** done by a system is work done by a system other than from volume change denoted  $W'$ .

**Proposition 4.2.3.** For reversible processes the effective work done is equal to the change in Gibbs free energy.

$$dW' = dG$$

**Proposition 4.2.4.** The entropy, volume, and chemical potential of a system in the isothermal–isobaric ensemble can be written in terms of the Gibbs free energy.

$$\sigma = - \left( \frac{\partial G}{\partial \tau} \right)_{P,N}, \quad V = - \left( \frac{\partial G}{\partial P} \right)_{\tau,N}, \quad \mu = - \left( \frac{\partial G}{\partial N} \right)_{\tau,P}$$

## 4.3 Enthalpy

For systems at constant pressure but not fixed temperature, there is another concept analogous to the Helmholtz free energy.

**Definition 4.3.1.** The **enthalpy** denoted  $H$  is minimized at equilibrium for a system at constant pressure.

$$H = U + PV$$

**Proposition 4.3.2.** For reversible processes the effective work done is equal to the difference in change in enthalpy and change in heat energy.

$$dW' = dH - dQ$$

**Proposition 4.3.3.** The temperature, volume, and chemical potential of a system in the isothermal–isobaric ensemble can be written in terms of the Gibbs free energy.

$$\tau = \left( \frac{\partial H}{\partial \sigma} \right)_{P,N}, \quad V = \left( \frac{\partial H}{\partial P} \right)_{\sigma,N}, \quad \mu = \left( \frac{\partial H}{\partial N} \right)_{\sigma,P}$$

## 4.4 Chemical Reactions

**Proposition 4.4.1.** The Gibbs free energy can be written in terms of the chemical potential and particles number.

$$G = N\mu$$

For a chemical reaction we often need to consider multiple species of particles that react with each other. To do this we will consider the total Gibbs free energy of the system.

**Proposition 4.4.2.** The total Gibbs free energy for a system of multiple particles is

$$G = \sum_j N_j \mu_j$$

**Definition 4.4.3.** The **chemical equation number**  $\nu$  is the sign and magnitude of  $dN$  relative to the other components of the reaction. For products  $\nu < 0$  and for reactants  $\nu > 0$ .

**Proposition 4.4.4.** Equilibrium for a system of multiple particles is reached when

$$\sum_j dN_j \mu_j = 0 = dG$$

$$\sum_j \nu_j \mu_j = 0$$

**Proposition 4.4.5. Law of Mass Action** - For the ideal gas model the equilibrium constant  $K(\tau)$  only depend on  $\tau$ .

$$K(\tau) = \prod_j n_j^{\nu_j} = \prod_j n_{Q,j}^{\nu_j} Z_{int,j}^{\nu_j} = \prod_j n_{Q,j}^{\nu_j} e^{-\nu_j F_j^{int}/\tau}$$