# PH2223 - Thermal and Statistical Physics

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## Chapter 1

## **Preliminaries**

#### 1.1 Introduction

## 1.1.1 Large Numbers - What is a mole?

Population of India:  $\approx 1.4 \times 10^9$  Indian Economy:  $\approx 4 \times 10^{12}$  USD

Number of N $_2$  molecules in 1kg of Nitrogen:  $\approx 10^{25}$ 

This number is too big. Instead of dealing with numbers this large. We will be dealing with averages for these large set of numbers.

Consider the addition of two numbers  $a_1$  and  $a_2$ , given they are of the same order of magnitude. As we increase the number of terms, the sum increases, but overall sum is not going to change by a significant value. As we approach 100 terms, another term added will only result in minor fluctuations in the sum.

We use the term mole as a unit to represent the number of particles in a system.

**Mole:** A mole is defined as the quantity of matter that contains as many entities as the number of atoms in exactly 12g of  $^{12}C$ . This number is represented as  $N_A$  and is approximated to:

$$N_A = 6.022 \times 10^{23}$$

**Thermodynamic Limit:** When the number of elements in our system increases to a number large enough such that the fluctuations in the sum is very little is known as the Thermodynamic Limit. This is the point where we can deal with averages and their distributions instead of precise values.

#### 1.1.2 Combinatorics

In the above examples, we are merely counting the number of objects present. But often times we will be dealing with the various ways in which the parameters of these objects can be changed and how that can affect the overall macroscopic system.

**Logarithm and Sterling's Approximation** When dealing with very large numbers we will be using logarithms(often base e) to make the large numbers that we have to deal with down to a size that is easier to understand. As we will be dealing with large numbers and their factorials, we will be using the Sterling's approximation to simplify the logarithms:

$$ln(n!) \approx n ln(n) - n$$

### 1.1.3 Properties of Gas

There are many properties that can be used to describe the state of a Gas. Eg: Volume V, Internal Energy U, Pressure P, Temperature T.

These properties are broadly classified as:

- 1. **Intensive Properties** Properties that are not affected by the size of the system. Eq. P,T
- 2. Extensive Properties Properties that scale with the size of system. Eg: V, U

#### 1.1.4 Ideal Gas

Experiments on gases show some of the relations between P, V and T

1. Boyle's Law A fixed amount of gas at a constant temperature obeys:

$$P \propto \frac{1}{V}$$

2. Charles' Law A fixed amount of gas at a constant pressure obeys:

$$V \propto T$$

where T is measure in Kelvin.

3. Gay-Lussac's Law A fixed amount of gas at a constant volume obeys:

$$P \propto T$$

These three laws can be combined to give the following relation:

$$PV \propto T$$

Now, if we consider that there are N molecules in the gas:

$$PV = Nk_bT$$

where  $k_b$  is the Boltzmann constant.

#### 1.2 Heat

#### 1.2.1 Definition

Heat is defined as the thermal energy in transit. Heat is never stored in objects. It is only energy that is stored. Heat naturally only flows from a body with higher temperature to a body with lower temperature. Though, when there is an external energy is provided, heat can flow from a colder body to a hotter body.

#### 1.2.2 Heat Capacity

Heat is not stored. But what Physics has conventionally called this Heat Capacity, so we will call it Heat Capacity.

**Heat Capacity** It is the amount of heat(energy) dQ that is required to raise the temperature of the system by a small amount dT.

Heat Capacity 
$$C = \frac{dQ}{dT}$$

Heat Capacity of the system C per unit mass is known as the Specific Heat Capacity c.

Often times the heat provided to the system isn't utilized fully just to increase temperature. There are often other constraints to the system, like if the heat is used to do work on the surroundings. In these cases, we will be using terms like Heat Capacity at constant pressure  $C_P$  or Heat Capacity at constant Volume  $C_V$ 

## 1.3 Probability

Probability is required in Statistical Mechanics because a lot of the phenomenon that occur predicted by the physics are often with a given with a statistical background. Eg: Probability of various macrostates of a system.

### 1.3.1 Discrete Probability Distributions

Discrete Random Variables take a finite (or countably infinite) values. Examples include the number of heads in a coin toss experiment, number of sibblings per person, etc. Let x be a discrete random variable, and  $x_i$  be the possible values of x. The probability of the random variable taking the value  $x_i$  is denoted by  $p_i$ . Some of the properties include:

1. Sum of probabilities of all random variables add up to 1:

$$\sum_{i} p_i = 1$$

2. Mean or expectation value of the random variable is defined as:

$$\langle x \rangle = \sum_{i} x_i p_i$$

3. Any function of x can be averaged as:

$$\langle f(x) \rangle = \sum_{i} f(x_i) p_i$$

### 1.3.2 Continuous Probability Distributions

Continuous Random Variables take values in a continuous range, i.e., they take uncountably infinite values. Examples include height of a person, time a train gets delayed by, etc. We define a Probability Distribution Function P(x) that says the random variable x has a probability of P(x)dx of being in the range [x, x + dx]. Some of the properties include:

1. The probability of the random variable being in the entire range is 1:

$$\int_{-\infty}^{\infty} P(x)dx = 1$$

2. The expectation value of the random variable is defined as:

$$\langle x \rangle = \int_{-\infty}^{\infty} x P(x) dx$$

3. Any function of x can be averaged as:

$$\langle f(x) \rangle = \int_{-\infty}^{\infty} f(x) P(x) dx$$