

STATISTICAL THERMODYNAMICS

M.SC. PART 2

PHYSICAL CHEMISTRY

PRESENTED BY

DR RENU NAYAR

DEPARTMENT OF CHEMISTRY

D.P.VIPRA COLLEGE ,BILASPUR CG

TOPIC ----ESSENTIALS OF THERMODYNAMICS NEEDED FOR LEARNING STATISTICAL MECHANICS

Discussion on statistical mechanics often begins with Thermodynamics--- WHY ?

Statistical Mechanics provides a microscopic basis of thermodynamics and meaning to such terms as entropy and free energy, which are otherwise rather hard to understand

Thermodynamics by itself is not useful because it does not have the capacity to generate absolute numbers needed to understand experiments.

For example, the first two laws define all sorts of relations between thermodynamic variables and functions (like entropy, free energy), but do not tell you how to calculate them. This deficiency is partly removed in the third law (which is the only “imperfect” thermodynamic law).

Ultimate goal of Statistical Mechanics

To describe thermodynamic behavior of macroscopic observables in terms of molecules and intermolecular potential

Thus, Quantum mechanics and Statistical Mechanics together form a complete, first principles, theoretical framework that should be able to explain the physical properties of systems.

Why a fully deterministic approach that is prescribed in classical mechanics is insufficient to describe a system of an Avogadro number of molecules ?

- Initially, it was assumed that one can use a detailed classical mechanical approach to achieve this goal. That is, given a system of N molecules with given intermolecular potential.
- In classical mechanics, the future evolution of the system is fully determined once the initial conditions are provided. This evolution is determined by equations of classical mechanics.
- Two alternate descriptions are provided by Newton's equations of motion and Hamilton's equations of motion. The former is expressed in terms of velocities and forces and is given by $\mathbf{F}_i = m_i \frac{d\mathbf{v}_i}{dt}$ Where \mathbf{F}_i is the force exerted on particle i , m_i is the mass and \mathbf{v}_i is the velocity of particle i .
- For systems with constraints, it may be more appropriate to start with Hamilton's equations of motion.
- Let us attempt to follow a classical mechanical approach to describe a system of an Avogadro number of molecules.
- Note that we cannot solve Newton's or Hamilton's equations exactly even for a three-body system.

- Using computers we can simulate motion (that is, trajectory) of a certain number, say a few thousand molecules. Secondly, even having obtained trajectory of our system i.e the positions and velocities of all the molecules we do not know what to do with such a huge amount of data.

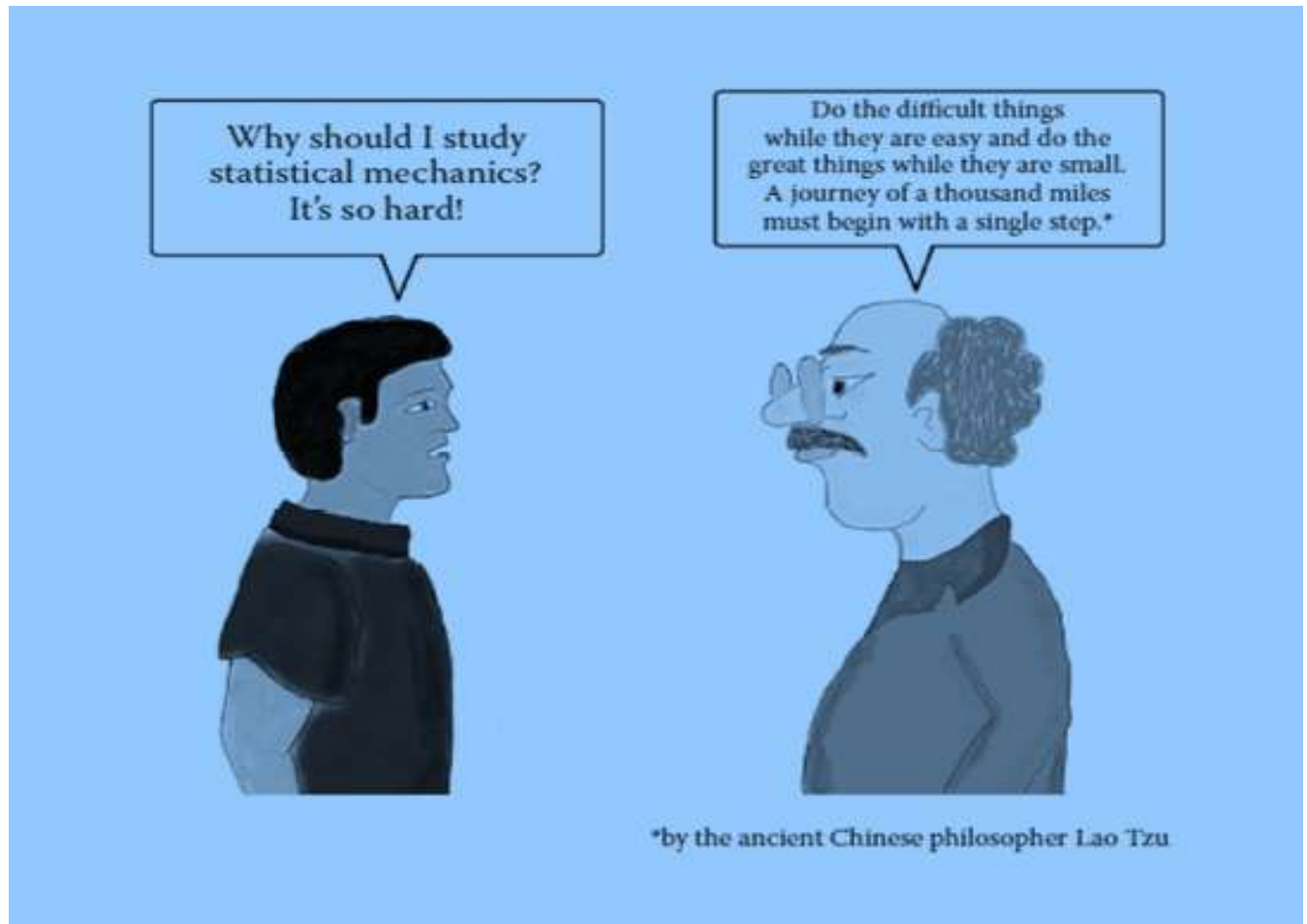
CONCLUSION: THE DETERMINISTIC APPROACH OF CLASSICAL MECHANICS IS INADEQUATE TO DESCRIBE THE MANY PARTICLE SYSTEM.

SOLUTION TO THE PROBLEM

- The statistical mechanical approach based on equations and concepts of classical mechanics but which abandons the deterministic approach. Instead, it uses a probabilistic approach.
- However, this translation from the description based on particles to a description based on probability distribution is highly non-trivial (MEANINGFUL).
- In fact, this change of theoretical description from a direct, deterministic, mechanical, particle based approach to a probability density based approach is carried out by invoking two basic assumptions or postulates which make the beginning of Statistical Mechanics.
- These two postulates (the *Ergodic hypothesis* and the *postulate of equal a priori probability*) allow us to go over to a probability based description where one can make sensible assumptions and

approximations, obtain closed form results which can be directly tested against experiments.

- At the first level, these assumptions allow one to develop a description for equilibrium properties without solving for particle trajectories.



Probability and Statistics

- Statistical Mechanics is formulated by using certain concepts of probability theory, it is imperative that students acquire certain basic knowledge of this theory.
- Probability theory in itself is a vast subject, but we for now require only certain elementary knowledge to understand the formulation of Statistical Mechanics.

➤ Why Probabilistic formulation needed?

- Statistical Mechanics deals with systems that consist of many degrees of freedom.
- Let us consider 1 cc of liquid water (that approximately weighs 1 g at 298K). It contains $(6.023 \times 10^{23})/18 = 3.34 \times 10^{22}$ water molecules.
- We know that each water molecule has nine degrees of freedom.
- So, we need to consider approximately 3×10^{23} degrees of freedom for a detailed microscopic description of structure (i.e., positions and orientations of water molecules) and dynamics (i.e., time evolution).
- If we at all desire for such a description. Clearly such a description is neither possible nor necessary, as we have already discussed earlier.

In Chemistry and Materials Science, the system sizes vary from nanoscale to macroscale. Even in nanoscale, except for extremely small sized systems, the systems of interest consist of millions of atoms and molecules.

- As also mentioned previously, we have no other option but to LEAVE a deterministic approach (Newtonian approach) and employ a probabilistic approach to make further progress.

- Such an approach was initiated by Maxwell and Boltzmann. Historically, the first probabilistic approach was pioneered by Maxwell, who derived the probability distribution function for the velocity.
- Subsequently, a more involved mathematical step towards a probabilistic approach was taken by Boltzmann.

CONCLUSION

Thus, in Statistical Mechanics we make the transition from a deterministic approach or language to a probabilistic description. The latter is developed in terms of **Distribution functions**. Our experimental observables are averages over such distributions. The distributions themselves are often not directly measured.

BASIC IDEA OF Distribution functions

- The basic idea behind a distribution function is that our observable (say, X) is intrinsically a random quantity. (**Values of Random variable depend on the outcomes of a random phenomenon**).
- Its value at a given moment of time is determined by positions and velocities of the constituent atoms and molecules of the system.
- If we could follow the instantaneous value of X with time we would see that its value fluctuates with time, around an average.
- As we shall see later, both the distribution function of instantaneous values of X and correlations between fluctuations contain important information about the system.
- We shall denote the probability distribution by $P(X,t)$.

RANDOM VARIABLE

- A random variable (X) is the outcome of an experiment.
- The same experiment repeated many times can give rise to (slightly) different values.
- The values can be discrete or continuous. For example, when we throw a die, the random variable is the “number of spots” on the side facing upward. The possible realizations are the numbers between 1 and 6, each with a probability of $1/6$. Similarly, in the tossing of an unbiased coin, we have two outcomes—head and tail—and the probability of each event is $1/2$. We denote the random variable by X and the possible outcomes by x .
- In many cases, x can be continuous, meaning all the values in a range, say $a \leq x \leq b$.
- An example of discrete distribution is the throwing of a die or coin
- Example of a continuous distribution is the distance travelled by different persons within a given time interval.
- Physical examples to emphasize the random, fluctuating nature of observables.
 - If we measure accurately the instantaneous pressure of a liquid in equilibrium with its vapor, we shall see that the pressure continuously fluctuates around an average value. The same holds for energy of a system kept at constant temperature, or the volume of a system kept at constant pressure. So, energy, pressure and volume are all random variables.
 - Another important example from the microscopic world is the number of nearest neighbors that a particle has within its first shell.

For a one component system of spherical atoms, this number varies between 9 and 13.

INFERENCE: In all the above examples, there exists an average, but the outcome can be different from the average and not predictable by an observer. One needs a probability distribution to describe the behaviors of the random variable.

Sample space

- Sample space is the collection of all the outcomes of an experiment. For example, when a coin is tossed once, the total numbers of outcomes (which are 2 in this case, either head or tail) are different when the same coin is tossed more than once.
- For example, if we toss the same coin twice, we have four possible outcomes: HH, HT, TH and TT (where H and T stand for head and tail, respectively).
- If the coin is tossed n times the possible outcomes are 2^n .
- Another illustrative example could be bus routes. Suppose you want to go from A to B via an intermediate stop at C. There are m ways by which you can go from A to C and another n ways to reach B from C. So the total number of ways one can go from A to B is $(m \times n)$. Thus the sample space consists of mn number of elements.
- Consider throwing a die. We have six outcomes, each of which is equally probable. If we now toss the die twice, we get $6^2 = 36$ possible outcomes. Then the probability of finding **three in the first toss and five in the second** will be $1/36$. But if we ask what is the probability of getting 3 in one and 5 in another toss separately, then the probability is $2/36$, as you have possibility to get three and five on both of the dice.

- Thus in probability an event could be a series of actions, and we need to consider all possible outcomes. This total set of outcomes of an event constitutes the sample space. The sample space allows us to define a probability distribution as we discuss below.

PROBABILITY DISTRIBUTION

- To characterize a random variable one first needs to obtain information about all the possible outcomes of elementary events (or, realizations) of the random variable.
- Then construct the probability of a given value as a possible outcome.
- When all the possible realizations (outcomes), do not form a discrete set but a continuum in R .
- Then we construct a continuous probability distribution function $P(X)$ or a probability density function $p(x)$. In the latter case we describe the probability of an outcome to have a value between x and $x + dx$ as $p(x)dx$.

The probability distribution is usually normalized. That is, it satisfies the following criteria

$$\int dx P(x) = 1$$

Joint Probability Distribution

- In many cases, outcomes of two events can be correlated. That is, the outcome of one event depends on the outcome of another.
- In such cases, probability of simultaneous occurrence of two events, namely A and B , is expressed by a joint probability distribution. The number of events can be generalized to any number.
- If two events A and B are completely uncorrelated, then the probability of the occurring of both will be simple multiplication of the probability of the occurring of those events individually.
- Joint probability of two events A and B is written as $P(AB)$. If both A and B are uncorrelated then joint probability of occurrence of A and B will be $P(AB) = P(A)P(B)$
- Explanation of this can be given from the previous example of throwing a die twice. Here getting a three in one die is not at all affected by the event of getting a two in the other one.

Conditional Probability

- However, our primary interest lies in correlation and in correlated events. For example we call a dense liquid a strongly correlated system because position of one molecule affects the probability of finding another molecule next to it. The idea of correlation among different events leads to *conditional probability*.
- Let us again consider two events A and B . We now ask the question: *given that an event A has already occurred, what is the probability of the occurrence of B ?* More precisely, if we know the value of the outcome of one experimental result, how does it impact our a priori knowledge of the outcome of a second experiment?

- **The two experiments need not be the same.**
- *For example, suppose we know that the age of a girl is 12 years. We want to infer her height. Another example is the following.*
- *Suppose Rafael Nadal won seven of the last 11 tennis matches against Roger Federer. What could be the possible outcome of the next match?*

The presence of correlation between the two events is measured by conditional probability. Note that in the presence of correlation among two events, the volume of the sample space becomes less (than in the absence of any correlation), because the outcome of one experiment partly determines that of the other. Conditional probability is symbolized as $P(B | A)$ which is defined as

$$P(B | A) = \frac{P(BA)}{P(A)}$$

If A and B are uncorrelated then conditional probability becomes the probability of the occurrence of B only as $P(BA)$ and then can be factorized into a multiplication of $P(A)$ and $P(B)$.