

Statistical Mechanics (SM)

↳ What is SM?

- The essential purpose of SM is to understand the behavior of large-scale macroscopic physical systems in terms of the laws of motion that govern their microscopic constituents.
- SM is the art of turning the microscopic laws of physics into a description of nature on a macroscopic scale.
- SM gives the dictionary that allows us to translate from the microscopic world where the laws of Nature are written to the everyday macroscopic world we are familiar with. This allows us to begin to address very basic questions about how matter behaves.

↳ A remarkable amount can be understood at the macroscopic level from the purely phenomenological science of thermodynamics, and the insight into this phenomenology that is provided by a statistical treatment of microscopic physics is of prime importance.

- There are many hundreds of laws of the phenomenological science of thermodynamics.

Examples: (1) Boyle's law & Charles law.

- (2) The Stefan-Boltzmann law telling how much energy a hot object emits.
- (3) Wien's Displacement law giving the color of the hot object.
- (4) Dulong Petit's law giving the amount of energy it takes to heat up a lump of stuff.
- (5) Curie's law tells you how a magnet loses its magnetism if you put it over a flame.

- Yet we know that these laws are not fundamental.
- In some cases, they simply follow from Newtonian Mechanics and a dose of statistical thinking.
- In other cases, we need to throw QM into the mix as well
- But all the cases can be derived from first principles.

- ↳ To a considerable extent, the general character of the laws of statistical physics does not depend on the mechanics (classical or quantum) which describes the motion of the individual particles in a body, but their substantiation demands a different argument in the two cases.
- ↳ The statistical laws resulting from the presence of a large no. of particles forming the body cannot in any way be reduced to purely mechanical laws.
- One of their distinctive features is that they cease to have meaning when applied to mechanical systems with a small no. of degrees of freedom
 - Thus, although the motion of systems with a very large no. of Dof obey the same laws of mechanics as that of systems consisting of a small no. of particles, the existence of many degrees of freedom results in laws of a different kind.
- ↳ The importance of statistical physics in many other branches of theoretical physics is due to the fact that in nature we continually encounter macroscopic bodies whose behavior cannot be fully described by the methods of mechanics alone and which obey statistical laws.

Macroscopic vs. Microscopic Systems ($10^{23} \neq 1$)

Microscopic Systems

Roughly of atomic dimensions or smaller ($\approx 10 \text{ \AA}$ or smaller)

Example: a molecule..

Macroscopic Systems

Large enough to be visible in the ordinary sense ($> 1\text{m}$, so that it can atleast be observed with a microscope using ordinary light.)

Example: consists of very many atoms or molecules (solid, liquid, gas, em-radiation)

↳ Interesting things happen when you throw 10^{23} particles together

↳ $10^{23} \neq 1 \Rightarrow$ More is different :

- There are key concepts that are not visible in the underlying laws of physics but emerge only when we consider a large collection of particles.

Example:- Temperature

- It is not a fundamental concept: it doesn't make much sense to talk about the temperature of an e^- .
- But it would be impossible to talk about Physics of the everyday world around us without mention of temperature.
- Above example illustrates the fact that the language needed to describe physics on one scale is very different from that needed on other scales.

- ↳ When one is dealing with a macroscopic system, one is, in general, not concerned with the detailed behavior of each of the individual particles constituting the system.
- ↳ We want answers to much more basic, almost childish, questions about the macroscopic system. Is it wet? Is it hot? What color is it? What happens if we squeeze it, pull it, heat it up?
- ↳ That is one is usually interested in certain macroscopic parameters which characterize the system as a whole, e.g., quantities like volume, pressure, magnetic moment, thermal conductivity, etc.
- ↳ The wavefunction of a macroscopic system very rarely captures the relevant physics because real macroscopic systems are not described by a single pure quantum state.

Why Statistical Mechanics if there are already Classical and Quantum Mechanics

↳ A box contains 10^{23} particles whose mass, charge and interactions are known. Also, known are all the fundamental laws of Nature.

Question:- What information can be given about the stuff in the box?

Classical Mechanics

Approach

Construct and integrate equations of motion of the system, equal to the number of its degrees of freedom.

Difficulties

- With a very large no. of DOF, the necessity of setting and solving the same no. of differential equations is impracticable.
- Even if we could integrate these equations in the general form, it would be completely impossible to substitute in the general solution the initial condition for the velocities and coordinates of all the particles.

Quantum Mechanics

Approach

Solve the time-independent Schrödinger equation $\hat{H}|\Psi\rangle = E|\Psi\rangle$. The Hamiltonian \hat{H} has a very large no. of degrees of freedom.

Difficulties

- Writing Schrödinger equation is typically not possible for 23 particles let alone 10^{23} particles.
- The energy eigenstates $|\Psi\rangle$ are very complicated objects since they contain information about what each of these particles is doing. They are called microstates.
- In practice, it is often extremely difficult to write down the microstate describing all these particles.

Bright Light in the Dark

- ↳ At first sight we might conclude from the difficulties that, as the no. of particles increases, so also must the complexity and intricacies of the properties of the mechanical system, and that no trace of regularity in the behavior of a macroscopic body.
- ↳ This is not so, however, when the no. of particles is very large, new types of regularity appear.

↳ Subsystems:-

Consider a macroscopic body or system of bodies, and assume that the system is closed, i.e., does not interact with any other bodies.

A part of the system, which is very small compared with the whole system but still macroscopic, may be imagined to be separated from the rest; clearly, when the no. of particles in the whole system is sufficiently large, the no. in the small part of it may still be very large. Such relatively small but still macroscopic parts will be called subsystems.

- ↳ A subsystem interacts in various ways with other parts of the system.
- ↳ Because of the very large no. of degrees of freedom of the other parts, these interactions will be very complex and intricate.

- ↳ As such the state of the subsystem considered will vary with time in a very complex and intricate manner.
- ↳ Fortunately, it is just this very complicated manner of variation of the state of subsystems which, though rendering the methods of mechanics inapplicable, allows a different approach to the solution of the problem.
- ↳ A fundamental approach of this approach is the fact, because of the extreme complexity of the external interactions with the other parts of the system, during a sufficiently long time the subsystem considered will be many times in every possible state.
- ↳ This may be more precisely formulated as follows:

$\Delta p \Delta q =$ small vol. of phase space of the subsystem corresponding to coordinates q_i and momenta p_i lying in short intervals $\Delta q_i \otimes \Delta p_i$.

$T =$ A sufficiently long time during which extremely intricate phase space trajectory passes many times through each such volume $\Delta p \Delta q$ of phase space.

$\Delta t =$ Part of the total time during which the subsystem was in the given vol. of phase space $\Delta p \Delta q$.

Let $\frac{\Delta t}{T}$ tends to some limit, let us say w .
 $T \rightarrow \infty$

$$\text{i.e., } \omega = \frac{L_t}{T} \frac{\Delta t}{T}$$

\Rightarrow This quantity may clearly be regarded as the probability that, if the subsystem is observed at an arbitrary instant, it will be in the given volume of phase space $d\mathbf{p}d\mathbf{q}$.

\Rightarrow On taking the limit of an infinitesimal phase volume ($d\mathbf{p}d\mathbf{q}$)

$d\omega =$ the probability of states represented by the points in the phase space volume of $d\mathbf{p}d\mathbf{q}$.

\Rightarrow we will be discussing those systems that have been left alone for some time.

This ensures that the energy and momentum in the system has been redistributed among the many particles and any memory of whatever special initial conditions the system started in has long been lost.

\Rightarrow For such cases

$$d\omega = \ell(\mathbf{q}, \mathbf{p}) d\mathbf{q} d\mathbf{p}$$

ℓ = "density" of the probability distribution in phase space

= Statistical distribution function

= distribution function

$\Rightarrow \int \ell d\mathbf{p}d\mathbf{q} = 1$ (Normalization Condition)

= Sum of the probabilities of all possible states must be unity.

⇒ The determination of the statistical distribution for any subsystem is in fact the fundamental problem of statistical physics.

⇒ P is independent of initial state of any other small part of the same system, since over a sufficiently long time the effect of this initial state will be entirely outweighed by the effects of the much larger remaining parts of the system.

P is independent of the initial state of the subsystem considered, since in time this part passes through all possible states, any of which can be taken as the initial state.

"Without having to solve the mechanical problem for a system (taking account of initial conditions), we can therefore find the statistical distribution for small parts of the system."

⇒ In speaking of "small parts" of a closed system, we must bear in mind that the macroscopic bodies with which we have to deal are usually themselves such "small parts" of a large closed system consisting of these bodies together with the external medium which surrounds them.

↳ Uses of Statistical Distribution

(1) We can calculate the probabilities of various values of any physical quantity which depends on the states of the subsystem (i.e., on the values of its coordinates q and momenta p).

(2) We can also calculate the mean value of any such quantity $f(q, p)$ as

$$\bar{f} = \int e(q, p) f(q, p) dq dp$$

i.e., by multiplying each of its possible values by the corresponding probability and integrating over all states.

Note:- The averaging w.r.t. the distribution (called statistical averaging) frees us from the necessity following the variation with time of the actual value of the physical quantity $f(q, p)$ in order to determine its mean value.

The latter is Rfa time averaging and is given as

$$\bar{f} = \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T f(t) dt$$

Statistical Independence

↳ Quasi-closed Subsystems

- Because subsystems are macroscopic bodies, the relative number of particles near the surface compared with the total number of particles in the subsystems is very small.
- Also, the particles which mainly take part in the interaction of a subsystem with the surrounding parts are those near the surface of subsystem.
- Therefore, the energy of interaction of a subsystem with the surrounding parts will be small in comparison with its internal energy.
- Thus, even though the subsystems are not closed (they are subject to continuous interaction with the remaining) parts of the system, we can still suppose that over not too long intervals of time they behave approximately as closed systems.
- Such weakly interacting are in short k/a quasi-closed.

↳ Statistical Independence

- Quasi-closed subsystems are regarded as statistically independent.
- Statistical Independence \Rightarrow The state of one subsystem does not affect the probabilities of various states of the other subsystems.
- For a composite subsystem consisting of two smaller subsystems 1 & 2, we have

$$d\omega_{12} = \ell_{12}(q_1, p_1, q_2, p_2) dq_1 dp_1 dq_2 dp_2$$

• Statistical Independence \Rightarrow

$$(1) d\omega_{12} = \ell_1(q_1, p_1) \ell_2(q_2, p_2) dq_1 dp_1 dq_2 dp_2 \\ = d\omega_1 \cdot d\omega_2$$

(2) $\ell_{12} = \ell_1 \cdot \ell_2$, where ℓ_1 & ℓ_2 are the distribution functions of the separate subsystems

(3) A similar relation is valid for a group of several subsystems provided, of course, that these subsystems together still form only a small part of the whole closed system.

$$(4) \underline{f_1 f_2} = \underline{f}_1 \cdot \underline{f}_2$$

(5) The converse statement is also true:

if the probability distribution for a compound system is a product of factors, each of which depends only on quantities describing one part of the system, then the parts concerned are statistically independent, and each factor is proportional to the probability of the state of the corresponding part.

Probabilistic Nature of Statistical Physics

- ↳ The deductions & predictions concerning the behavior of macroscopic bodies which are made possible by statistical physics are probabilistic.
- ↳ In this respect statistical physics differs from (classical) mechanics, the deductions of which are entirely deterministic.
- ↳ In particular, the probabilistic nature of the results of classical statistics is not an inherent property of the objects considered, but simply arises from the fact that these results are derived from much less information than would be necessary for a complete mechanical description (the initial values of the coordinates and momenta are not needed).
- ↳ Mean Square Deviation of a physical quantity $f(q, p)$

$$\begin{aligned}\langle (\Delta f)^2 \rangle &= \int (f - \bar{f})^2 \ell(q, p) dq dp \\ &= \int (f^2 + \bar{f}^2 - 2f\bar{f}) \ell(q, p) dq dp \\ &= \bar{f}^2 + \bar{f}^2 - 2\bar{f}^2 \\ &= \bar{f}^2 - \bar{f}^2\end{aligned}$$

↳ The ratio $\langle (\Delta f)^2 \rangle / f^2$ is called the relative fluctuation of the quantity f . The smaller this ratio is, the more negligible is the proportion of time during which the body is in states where the deviation of f from its mean value is a considerable fraction of the mean value.

Additive nature of Physical Quantities

- ↳ Majority of quantities of physical interest are additive.
- ↳ This property is a consequence of the fact that the various parts of a body are quasi-closed systems, and signifies that value of such a quantity for the whole body is the sum of its values for the various (macroscopic) parts of the body.
- ↳ For example, since the internal energies of these parts are large compared with their interaction energies, it is sufficiently accurate to assume that the energy of the whole body is equal to the sum of the energies of its parts.

Variation of Relative Fluctuation with Particle Number

• f = Additive Physical Quantity

- Macroscopic System of n # of particles is divided into N equal subsystems and the subsystems are observed over not too long intervals of time (i.e., they can be treated approximately as closed and thence statistically independent).

$$\Rightarrow f = \sum_{i=1}^N f_i, \\ \bar{f} = \frac{1}{N} \sum_{i=1}^N \bar{f}_i.$$

- Increasing particle # by a factor, say K , increases N by K as well \Rightarrow increases \bar{f} by K as well.

$$\therefore \bar{f} \propto n$$

$$\begin{aligned} \overline{(\Delta f)^2} &= \overline{(f - \bar{f})^2} \\ &= \overline{(\sum f_i - \sum \bar{f}_i)^2} \\ &= \overline{(\sum \Delta f_i)^2} \\ &= \sum_i \overline{\Delta f_i^2} + 2 \sum_{\substack{i, k \\ i \neq k}} \overline{\Delta f_i \Delta f_k} \end{aligned}$$

$$= \overline{\sum \Delta f_i^2} + 2 \overline{\sum \Delta f_i \Delta f_R}$$

But as per eqn. (1), $\overline{\Delta f_i \Delta f_R} = \overline{\Delta f_i} \cdot \overline{\Delta f_R}$.

Also, $\overline{\Delta f_i} = \overline{\Delta f_R} = 0$ (since mean of absolute deviation = 0 always)

$$\therefore \overline{(\Delta f)^2} = \overline{\sum \Delta f_i^2}$$

For the whole system

$$\mathcal{L} = \mathcal{L}_1(q_1, p_1) \mathcal{L}_2(q_2, p_2) \dots \mathcal{L}_N(q_N, p_N)$$

$$\therefore \overline{(\Delta f)^2} = \overline{\sum \Delta f_i^2} = \int \overline{\sum \Delta f_i^2} \mathcal{L} dq dp$$

$$= \sum \overline{\Delta f_i^2}$$

$$\Rightarrow \overline{(\Delta f)^2} \propto N$$

$$dq/dp \equiv dq_1 dq_2 \dots dq_N \times \\ dp_1 dp_2 \dots dp_N$$

$\propto n$ as $N \propto n$

$$\Rightarrow \frac{\sqrt{\overline{(\Delta f)^2}}}{f} \propto \frac{n}{\sqrt{n}} \propto \frac{1}{\sqrt{n}}$$

Conclusion :- The relative fluctuation of any additive quantity $f \propto \frac{1}{\sqrt{n}}$

⇒ When n is sufficiently large, the quantity f itself may be regarded as constant in time & equal to its mean value.

Thermodynamics

- ↳ It is a consequence and reflection of the symmetries of nature.
- ↳ It is what remains after collisions b/w the many dof of macroscopic systems randomize and destroy most of the coherent behavior.
 - The quantities which cannot be destroyed, due to underlying symmetries of nature and their resulting conservation laws, give rise to the state variables upon which the theory of thermodynamics is built.
- ⇒ Thermodynamics is therefore a solid & sure foundation upon which we can construct theories of matter out of equilibrium.
- ↳ The science of thermodynamics began with the observation that matter in the aggregate can exist in macroscopic states which are stable and do not change in time.
 - These stable "equilibrium" states are characterized by definite mechanical properties, such as color, size, and texture, which change as the substance becomes hotter or colder (Changes its temperature).
 - However, any given equilibrium state can always be reproduced by bringing the substance back to the same state.
 - Once a system reaches its equilibrium state, all changes cease and the system will remain forever in that state unless some external influence acts to change it.
 - This inherent stability and reproducibility of the equilibrium

states can be seen everywhere in the world around us.

- ↳ Thermodynamics has been able to describe, with remarkable accuracy, the macroscopic behavior of a huge variety of systems over the entire range of experimentally accessible temperatures (10^{-4} K to 10^6 K).
- ↳ It provides a truly universal theory of matter in aggregate.
- ↳ Because thermodynamics is based on the common experience of macroscopic observations, it has a generality unequalled in science.
 - "Classical thermodynamics," Einstein remarked, "... is the only physical theory of universal content ... which ... will never be overthrown" (Schlipp, 1949)
- ↳ The laws of thermodynamics deal with processes not structures. Therefore, no theory of matter is contained in these laws.
- ↳ There are several approaches to the formulation of thermodynamics.
 - Most common is the phenomenological approach, based on observation.
 - A phenomenological theory is one in which initial observations lead to a law.
- ↳ Laws are seldom, if ever, formulated in terms of primary measurements because such formulations could lead to cumbersome statements.
 - Rather, concepts are introduced that, as a result of the primary measurements, behave in a characteristic way, giving rise to new concepts, in terms of which laws are expressed concisely and take

on a simpler form.

- ↳ Equilibrium:- If the macroscopic parameters of an isolated system do not vary in time, then one says that the system is in equilibrium.
 - If a closed macroscopic system is in a state such that in any macroscopic subsystem the macroscopic physical quantities are to a high degree of accuracy equal to their mean values, the system is said to be in a state of statistical equilibrium (or thermodynamic or thermal equilibrium).
 - It is what remains after collisions b/w the many Dof of macroscopic systems randomize and destroy most of the coherent behavior.
 - If an isolated system is not in equilibrium, the parameters of the system, will in general, change until they attain constant values corresponding to some final equilibrium condition.
 - Equilibrium situations can clearly be expected to be amenable to simpler theoretical discussion than more-general time dependent non-equilibrium situations.
- ↳ Macroscopic systems (like solids, liquids, or gases) began first to be systematically investigated from a **macroscopic** **phenomenological** point of view. The laws thus discovered formed the subject of "thermodynamics".
- ↳ Thermodynamics is historically the oldest discipline.

↳ Disadvantage of Thermodynamics:-

- It makes very general statements concerning relationships b/w the macroscopic parameters of the system in equilibrium.
- The strength of this method is its great generality, which allows it to make valid statements based on a minimum number of postulates without requiring any detailed assumptions about the microscopic (i.e., the molecular) properties of the system.
- The strength of the method implies its weakness:
Only relatively few statements can be made on such general grounds, and many interesting properties of the system remain outside the scope of the method.
- Statistical mechanics on the otherhand yields all the results of thermodynamics plus a large number of general relations for calculating the macroscopic parameters of the system from a knowledge of its microscopic constituents. This method is one of great beauty and power.

Unified and Modern point of view of Thermodynamics Statistical Mechanics & Kinetic Theory

- ↳ On this point of view, entire discussion is based on the premise that all macroscopic systems consist ultimately of atoms obeying the laws of quantum mechanics.
- ↳ A combination of these microscopic concepts with some statistical postulates then leads readily to some very general conclusions on a purely macroscopic level of description.
- ↳ These conclusions are valid irrespective of any particular models that might be assumed about the nature of interactions of the particles of the systems under consideration; they possess, therefore, the full generality of the classical laws of thermodynamics.
- ↳ Indeed, they are more general, since they make clear that the macroscopic parameters of a system are statistical in nature and exhibit fluctuations which are calculable and observable under appropriate conditions.
- ↳ The customary approach of developing thermodynamics is based along purely macroscopic lines. This approach, however, has the following disadvantages:
 - difficult
 - delicate
 - unnatural to many physics students
 - the significance of the fundamental concept of entropy is very hard to grasp.

- ↳ The microscopic atomic theory alongwith some elementary statistical ideas following gains are achieved:
- (a) instead of spending much time discussing various arguments based on heat engines and cleverly chosen cycles, one can introduce to the student at an early age to statistical methods which are of great and recurring importance throughout all of physics.
 - (b) the microscopic approach yields much better physical insight into many phenomena and leads to a ready appreciation of the meaning of entropy.
 - (c) Much of modern physics is concerned with the explanation of macroscopic phenomena in terms of microscopic concepts. Traditional teaching of statistical mechanics and thermodynamics as distinct subjects has often left students with their knowledge compartmentalized and has also left them ill-prepared to accept newer ideas, such as spin temperature or negative temperatures, as legitimate and natural.
 - (d) Since a unified presentation is more economical, conceptually as well as in terms of time, it permits one to discuss more material and some more modern topics.

Thermodynamic Potentials

Response Functions

Entropy



