Statistical description of systems of particles

• **Specification of the state of the system** – Example: the uppermost face of a dice after a throw.

• **Statistical ensemble** – Instead of focusing on a single experiment, we consider an ensemble of such experiments; example: the dice is thrown 10 times and the outcome is monitored in order to evaluate the probability of occurrence of it.

• **Basic postulate about apriori probabilities** – Example: the probabilities are equal than any of the six faces of the die is found uppermost: it does not contradict the laws of mechanics.

• **Probability calculations** – Example: theory of probability is applied in order to predict the outcome of any experiment involving dice.
Microscopic state of the system

**Quantum mechanics:** enumerate the set of $f$ quantum numbers of the system and assign a label to identify each of them. Example: for a system of $N_A$ spin-particles (fixed in position) a microscopic state is the set of the $f=N_A$ projections of the angular moment of the single particles ($m_z=-1/2,1/2$).

**Classical mechanics:** we specify the coordinates $(q_1, q_2, \ldots, q_f)$ and momenta $(p_1, p_2, \ldots, p_f)$ in a $2f$-dimensional phase space, taking care of the Heisenberg uncertainty principle ($\delta q \delta p \geq \hbar$). Then, every cell exploiting the lower bound of the uncertainty principle in that space, is a possible state of the system. Example: for a system of $N$ particles, $f=3N$.

$f$ is the number of degrees of freedom of the system.

lecture 15
Statistical ensemble

The evolution of a system in a microscopic state is completely deterministic both in quantum and classical mechanics. However, such information cannot be made available for a system with a large number of degrees of freedom.

We consider a large number of identical systems (ensemble), all prepared subject to different macroscopic conditions (pressure, temperature, magnetic moment,..) and we inquiry what is the fraction of elements of the ensemble which are characterized by the same macroscopic parameter (accessible states), or, what is the probability of occurrence of a particular value of the macroscopic parameter.

The aim of the theory will be to predict the probability of occurrence in the ensemble of a “macrostate” (a particular value of the macroscopic parameter, or a thermodynamic state) on the basis of some basic postulates.

Example: three spin-1/2 particles in a uniform magnetic field H.

Phase space: microstate

Macrostate
Basic postulate

What is the probability of finding the system in one of the accessible, microscopic states?

An isolated system at thermodynamic equilibrium is equally likely to be in any of its accessible states.

Γ space: 6N dimensional space of coordinates and momenta. Let us consider a system with N particles, inside a volume V and with energy between E and E + ΔE.

\[
\frac{\partial \mathcal{H}(p, q)}{\partial p_i} = \dot{q}_i, \quad \frac{\partial \mathcal{H}(p, q)}{\partial q_i} = -\dot{p}_i
\]

\[
\rho(p, q, t) \, d^{3N}p \, d^{3N}q = \text{no. of representative points contained in the volume element } d^{3N}p \, d^{3N}q \text{ located at } (p, q) \text{ in } \Gamma \text{ space at the instant } t
\]

Systems in the ensemble are distributed uniformly over the accessible states

\[
\frac{\partial \rho}{\partial t} + \sum_{i=1}^{3N} \left( \frac{\partial \rho}{\partial q_i} \frac{\partial \mathcal{H}}{\partial p_i} - \frac{\partial \mathcal{H}}{\partial q_i} \frac{\partial \rho}{\partial p_i} \right) = 0
\]

\[
\rho(p, q) = \rho'(\mathcal{H}(p, q)) \rightarrow \frac{\partial}{\partial t} \rho(p, q) = 0
\]

Liouville Theorem
Approach to equilibrium

Whatever is the initial state of the system, it will go through a non-equilibrium process aimed to reach the equilibrium state, which is the thermodynamic state where its distribution over the microscopic accessible states is uniform. From a more fundamental point of view this is a consequence of the H-Theorem by Boltzmann.

The fundamental postulate in quantum-mechanics: the probability that the system is in a quantum state $r$ (eigenstate of the Hamiltonian) is $P_r = |a_r|^2$, where $a_r$ is the complex probability amplitude of state $r$. At equilibrium $P_r$ is the same for all the possible quantum states $r$, and the related probability amplitudes differ only for random phase factors.
Probability calculations

Given an isolated system with an energy between $E$ and $E + \delta E$, $\Omega(E)$ is the total number of states in that range, and $\Omega(E; y_k)$ is the number of states for which the parameter $y$ (pressure, magnetic moment, ..) assumes the value $y_k$.

$$P(y_k) = \frac{\Omega(E; y_k)}{\Omega(E)}$$

$$y_k = \frac{\sum \Omega(E; y_k)y_k}{\Omega(E)}$$
Behaviour of the density of states

Consider a system with \( f \) degrees of freedom, so that \( f \) quantum numbers are necessary to specify each of its possible states. Let \( E \) be the energy measured from the fundamental state and \( \Phi(E) \) the total number of states with energy lower than \( E \). \( \Phi(\epsilon) \) is the counterpart of \( \Phi(E) \) for the quantum number associated to a particular degree of freedom.

\[
\Phi_1 \propto \epsilon^\alpha \quad (\alpha \approx 1) \quad \epsilon \approx \frac{E}{f} \quad \Phi(E) \approx [\Phi_1(\epsilon)]^f
\]

\[
\Omega(E) = \Phi(E + \delta E) - \Phi(E) = \frac{\partial \Phi}{\partial E} \delta E
\]

\[
\Omega(E) \approx f \Phi_1^{-1} \frac{\partial \Phi_1}{\partial \epsilon} \frac{1}{f} \delta E = \Phi_1^{-1} \frac{\partial \Phi_1}{\partial \epsilon} \delta E
\]

The number of possible states accessible to the system is a rapidly increasing function of the energy for macroscopic systems.
Behaviour of the density of states

\[ \ln \Omega = (f - 1) \ln \Phi_1 + \ln \left( \frac{\partial \Phi_1}{\partial \epsilon} \delta E \right) \approx 1 \]

\[ \ln \Omega \approx f \ln \Phi_1 \leq f \]

\[ \Omega \approx \Phi_1' \propto E' \]

In the last order of magnitude expression, we assumed \( \alpha = 1 \), since our order of magnitude is not affected if \( \alpha \) is of the order of \( f \).
Material for this lecture

Reif’s book: pages 47-63