

# Recapitulation

Last time we covered:

1. Thermodynamics and Theory of Gas
2. Interaction and Transition
3. Spin Model
4. Phase Space

Today, we will review some relevant concepts in quantum mechanics as they pertain to phase space and explore some other topics in statistical physics regarding how to average behavior, these are known as the Gibbs Ensemble which is a conceptual idea of replicating a system many times and then treating the average of the ensemble as representative of the system. We will visit important postulates as well as different averaging conceptual frames that are important for different system constraints.

1. Statistical Physics Postulate
2. Microcanonical Ensemble
3. Canonical Ensemble
4. Grand Canonical Ensemble

## Gibbs Ensemble

A Gibbs ensemble is an ensemble (collection) of independent replicas of the system. These replicas are each autonomous, they do not have to be in the same state (i.e., point in phase space); so together they occupy a distribution of states in phase space. From these arrangements, averaging will provide macroscopic physics quantities. The ensemble of replicas is depicted by a distribution of points in the area  $\Gamma(U)$  (e.g., the set of all states that have the same internal energy  $U$ —the *level set* of  $U$ ) of the phase space or by a continuous (but not necessarily uniform) density of states  $\rho(\{p_i\}, \{q_i\}, t)$  that can be calculated algebraically. Because each state that enters a small region in phase space must have come from another neighboring region in phase space, there is a conservation law for the density of states. The density of states evolves like an incompressible fluid—the phase space volume remains constant. This result is from mechanics, and is known as Liouville's theorem.

$$\frac{\partial \rho}{\partial t} + \vec{\nabla} \cdot (\vec{v} \rho) = 0 \quad (1)$$

where  $\vec{\nabla}$  is the differentiable operator on the  $3N$  momentum and  $3N$  position vectors.

$$\vec{v} = (\dot{p}_1, \dots, \dot{p}_{3N}, \dot{q}_1, \dots, \dot{q}_{3N}) \quad (2)$$

the equation of continuity becomes

$$-\frac{\partial \rho}{\partial t} = \sum_{i=1}^{3N} \left[ \frac{\partial}{\partial p_i} (\dot{p}_i \rho) + \frac{\partial}{\partial q_i} (\dot{q}_i \rho) \right] \quad (3)$$

$$-\frac{\partial \rho}{\partial t} = \sum_{i=1}^{3N} \left[ \frac{\partial \rho}{\partial p_i} (\dot{p}_i) + \frac{\partial \rho}{\partial q_i} (\dot{q}_i) \right] + \sum_{i=1}^{3N} \rho \left[ \frac{\partial \dot{p}_i}{\partial p_i} + \frac{\partial \dot{q}_i}{\partial q_i} \right]$$

The last term equals to zero (this follows from conservation of energy, and the principle of least action and is known as the Hamilton equation—the details are a subject of an advanced course in mechanics or calculus of variations).

$$\frac{d\rho}{dt} = 0 \quad (4)$$

This indicates that the distribution of systems over all of the states remains then unchanged in time, i.e., one has an equilibrium situation. We will use this density to evaluate the value of average of a physical quantity  $A(\{p_i\}, \{q_i\}, t)$

$$\langle A \rangle = \int A(\{p_i\}, \{q_i\}) \rho(\{p_i\}, \{q_i\}, t) dq_i dp_i \quad (5)$$

where  $\rho$  is normalized on the phase space:

$$\int \rho(\{p_i\}, \{q_i\}, t) dq_i dp_i = 1 \quad (6)$$

## Statistical Physic Postulate

The first postulate stipulates that all microstates (or points in phase space) of an isolated system (i.e., at  $U$  is constant) are accessible and equiprobable (i.e., they are visited with equal frequency). if it is not the case, the system is out of equilibrium and will evolve to satisfy this condition. Mathematically, this first postulate can be written as

$$\begin{aligned} \rho(\{p_i\}, \{q_i\}) &= \text{constant in } \Gamma(U) \\ \rho &= 0 \quad \text{anywhere else} \end{aligned} \quad (7)$$

The second postulate stipulates that at a time  $t$ , a system at equilibrium can only have one microstate and if the system is observed for a very long time, we find that the time spent in each microstate is the same. It is the ergodic hypothesis:

$$\bar{A} = \lim_{t \rightarrow \infty} \frac{1}{t} \int_0^t A dt = \int_{\Gamma(U)} A(\{p_i\}, \{q_i\}) \rho(\{p_i\}, \{q_i\}) dp_i dq_i = \langle A \rangle \quad (8)$$

It is the counting and averaging of  $\Omega(U)$  that permit calculations of any macroscopic physical quantity,  $A$  in certain areas  $\Gamma(U)$  of the phase space. This will provide the links that exist between the microscopic and macroscopic viewpoints.

In the following, we will simplify the discussion by considering the probabilities of occurrence  $P_i$  of each microstate  $i$  instead of using the continuum density  $\rho$ . The average of the ensemble will be:

$$\langle A \rangle = \sum_i P_i A_i \quad (9)$$

## Microcanonical Ensemble

The microcanonical ensemble is a thermally and mechanically isolated system, e.g., a system with a given internal energy  $U$ . There are no exchanges of matter, work, or heat with its environment.

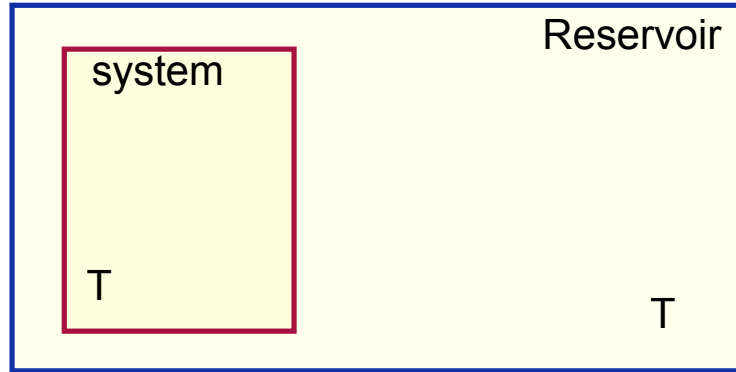


Figure 0-1: The system is isolated from its environment..

In this case,  $U$ ,  $N$ , and  $V$  are constants. The first postulate implies an equiprobability of the different microstates  $i = 1, \dots, \Omega$ . The probability  $P_i$  to find the system in its microstate  $i$  is then given by:

$$P_i = \frac{1}{\Omega} = \exp\left(-\frac{S}{k_B}\right) \quad (10)$$

$S$  is then given by

$$S = k_b \ln \Omega \quad (11)$$

For an isolated system (constant  $U$ ), the enumeration of microstates gives the entropy  $S$ . For simple systems, it is possible to make an exact count of such microstates of constant  $U$ ; for example, it is possible symbolically calculate the entropy of a perfect gas—this leads to the law of Sakur-Tetrode, derived from the equations of state. We will revisit this calculation in the canonical ensembles.

The microcanonical ensemble gives a manner to calculate the mean value of a physical quantity  $A$  via

$$\langle A \rangle = \sum_{i=1}^{\Omega} A_i P_i = \frac{1}{\Omega} \sum_{i=1}^{\Omega} A_i \quad (12)$$

This average value corresponds to the equilibrium value. Furthermore, one can consider small deviations about the average (equilibrium value) and calculate the the fluctuations  $(\Delta A)^2 = \langle A^2 \rangle - \langle A \rangle^2$  of a macroscopic quantity about its average.

$$\langle A^2 \rangle - \langle A \rangle^2 = \frac{1}{\Omega} \sum_{i=1}^{\Omega} (A_i^2 - \langle A \rangle^2) \quad (13)$$

## Canonical Ensemble

When the system can exchange heat with a reservoir, but not work and matter, there is a larger number of microstates. We have to account for the microstates  $1 \leq i \leq \Omega(U_j)$  accessible to the system which has a given energy  $U_j$ . This is known as the *canonical ensemble*

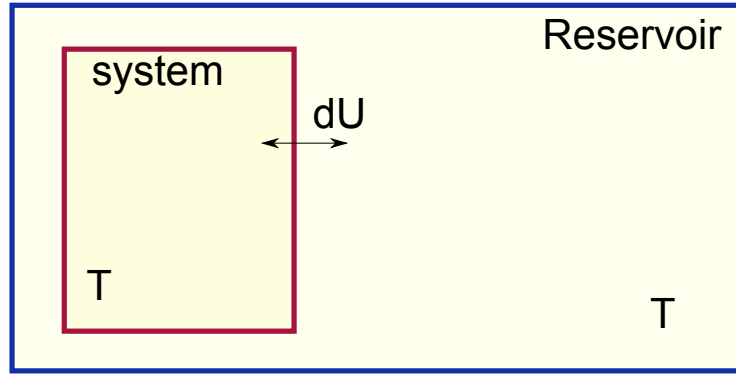


Figure 0-2: The system is in contact with the reservoir. The heat is exchanged between the system and the reservoir.

The reservoir maintains the temperature  $T$  constant and the total energy,  $U_0 = U_j + U_T$ , of the system plus its reservoir is constant. The total number of microstates  $\mathcal{N}$  accessible for the system and the reservoir will be given by

$$\mathcal{N}(U_0) = \Omega(U_j)\Omega_T(U_0 - U_j) \quad (14)$$

which is constant with regard to all the possible variations  $U_j$  because the total energy is constant. The probability  $P_{ij}$  to find the system in the microstate  $i$  of the energy  $U_j$  will be proportional to

$$P_{ij} \propto \frac{1}{\Omega(U_j)} \quad (15)$$

at equilibrium; this probability is also proportional to

$$P_{ij} \propto \Omega_T(U_0 - U_j) \quad (16)$$

e.g., to the number of microstates accessible to the thermostat. The normalization requirement on probabilities leads to

$$P_{ij} = \frac{\Omega_T(U_0 - U_j)}{\sum_j \sum_i \Omega_T(U_0 - U_j)} \quad (17)$$

The thermostat that many more degrees of freedom than the system ( $N_j/N_T \ll 1$ ) as well as  $U_j \ll U_0$ , thus

$$\ln \Omega_T(U_0 - U_j) = \ln \Omega_T(U_0) - \left( \frac{\partial \ln \Omega_T}{\partial U} \right)_{U=U_0} U_j + \dots \quad (18)$$

The partial derivative of the first order is  $1/k_B T$  ( $k_B$  is the Boltzmann constant or  $R/N_{avg}$ ). We have

$$\begin{aligned} \ln \Omega_T(U_0 - U_j) &= \ln \Omega_T(U_0) - \frac{U_j}{k_B T} \\ \Omega_T(U_0 - U_j) &= \Omega_T(U_0) \exp\left(-\frac{U_j}{k_B T}\right) \end{aligned} \quad (19)$$

The probability  $P_{ij}$  of a particular microstate  $ij$  is

$$P_{ij} = \frac{1}{Z} \exp\left(-\frac{U_j}{k_B T}\right) \quad (20)$$

where  $Z$  is the quantity that normalizes the probabilities.  $Z$  is considered the most important quantity in statistical thermodynamics, because it can be used to derive so many quantities.

$$Z = \sum_j \sum_i \exp\left(-\frac{U_j}{k_B T}\right) \quad (21)$$

This function is called *partition function*. It is a function of  $T$ ,  $V$ , and  $N$ . *This function plays a very important role.*

In the *canonical ensemble*, there is a statistical weight associated at each microstate. This statistical weight is the exponential of the internal energy normalized by the thermal agitation  $k_B T$ . This last term is the energy term associated with the *Boltzmann constant*,  $k_B$ . We may note that at high temperature, all the microstates have the same probability of occurrence whatever the energy of these configurations. At low temperatures, the states with low energy are favored. *This result should be familiar: nature prefers that a system minimize its energy at low temperatures, and maximize its entropy at high temperatures.*