

## Statistical Thermodynamics

Lecture notes by Dr. Sudeep Punathanam

### Introduction

*Statistical Mechanics* is the study of macroscopic phenomena from a microscopic point of view. Statistical Mechanics helps us to understand, explain and predict macroscopic behavior of a collection of entities (e.g. molecules) given the microscopic behavior (e.g. inter-molecular interactions). The branch of statistical mechanics that deals with equilibrium thermodynamics behavior (e.g. pressure, entropy, free energy) is called *Statistical Thermodynamics*.

Only certain problems in statistical thermodynamics are exactly solvable (e.g. ideal gas, Einstein crystal, Ising model in one and two dimensions, etc.). Computer simulations provide exact numerical results for problems that are soluble by approximate methods or might be quite intractable.

Since computer simulations give exact results for a given model, these can be used to test the predictions of theories. Historically, computer simulations have been able to discriminate between well-founded approaches (integral equation theories) and ideas that are plausible but less successful (old cell theories of liquids). Computer simulation results can also be directly compared with experimental results. In such cases, the results can help in validating the molecular model used in the simulations. With a good model, the simulator can offer new information about the system, which are difficult or impossible to access experimentally and thus assist in interpreting new experimental results.

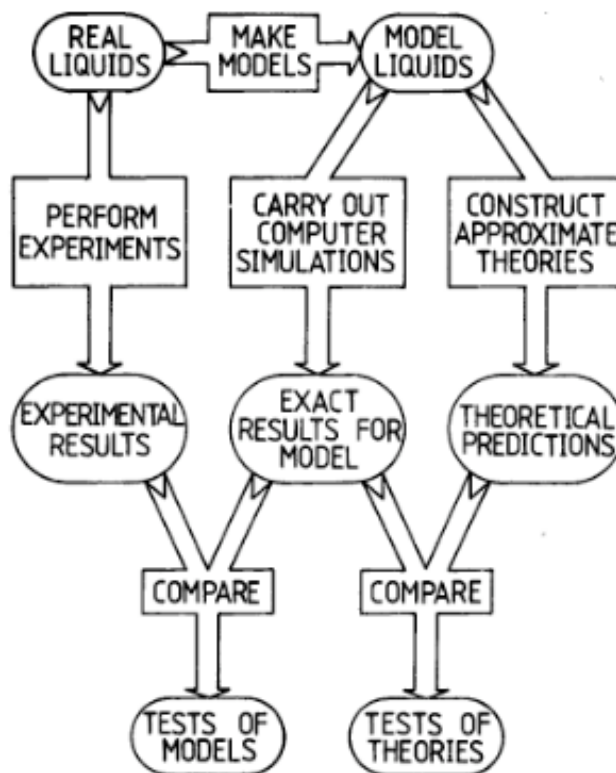


Figure 1: The connection between theory, experiments and computer simulations

## Concept of Ensembles

The state of a macroscopic system can be specified by few properties. For example, a pure liquid can be described completely by its mass, pressure and temperature. However, for each macroscopic state, there exist a large number of microscopic states corresponding to it. For quantum systems, each microscopic state is described by the eigenfunction obtained by solving the Schrodinger wave equation. For classical systems, the positions and momenta of all its constituent molecules describe each microscopic state. *An ensemble of systems* is a collection of various microscopic states of the system that correspond to the single macroscopic state of the system whose properties we are investigating.

Depending upon the thermodynamic environment of the system, we can create various representative ensembles. The commonly encountered ensembles are given below

Type of ensemble	Constant variables	Description
Microcanonical	N, V, E	Isolated system
Canonical	N, V, T	Closed isothermal system
Grand-canonical	$\mu$ , V, T	Open isothermal system
Isothermal-isobaric	N, P, T	Closed isothermal-isobaric system

## Time averaging versus Ensemble averaging

Suppose we wish to determine experimentally the value of a mechanical property (e.g. pressure, energy) of a system. Let us denote this property by the variable  $M$ . In general, the instantaneous value of  $M$  will depend on positions,  $\mathbf{r}^N$ , and momenta,  $\mathbf{p}^N$ , of the  $N$  particles of the system. The experimentally measured value is the time-averaged value of  $M(\mathbf{r}^N(t), \mathbf{p}^N(t))$ .

$$\langle M \rangle_{\text{time}} = \lim_{\tau \rightarrow \infty} \frac{1}{\tau} \int_0^{\tau} M(\mathbf{r}^N(t), \mathbf{p}^N(t)) dt$$

Another way of determining the value of  $M$  is through averaging over the various systems in the representative ensemble. Thus we obtain the ensemble-averaged value of  $M$  given as

$$\langle M \rangle_{\text{ens}} = \iint d\mathbf{r}^N d\mathbf{p}^N M(\mathbf{r}^N, \mathbf{p}^N) \rho(\mathbf{r}^N, \mathbf{p}^N),$$

where  $\rho(\mathbf{r}^N, \mathbf{p}^N)$  is the probability density distribution of finding a system in the ensemble having a configuration with momenta  $\mathbf{p}^N$  and positions  $\mathbf{r}^N$ .

## Postulates

*Postulate I:*

*The long time average of a mechanical variable  $M$  in the thermodynamic system of interest is equal to the ensemble average of  $M$ , in the limit as the number of systems of the ensemble become infinitely large, provided that the systems of the ensemble replicate the thermodynamic state and environment of the actual system of interest.*

The first postulate tells us that we can replace the time average with an average over instantaneous values for all the systems in the ensemble. It applies to all types of ensembles. Thus it is not necessary to follow the time evolution of the system in order to obtain the values for various mechanical properties. However, the postulate by itself does not help us to calculate the ensemble averages since no information is available about the probability distribution of the various microscopic states in the ensemble. Such information can be obtained by the application of the second postulate.

*Postulate II:*

*In an ensemble representative of an isolated thermodynamic system, the systems of the ensemble are distributed uniformly, that is, with equal probability or frequency, over the possible quantum states consistent with the specified values of  $N$ ,  $V$  and  $E$ .*

The second postulate applies only to the microcanonical ensemble. It is also known as postulate of equal *a-priori* probability. It states that the probability density  $\rho$  is uniform in the microcanonical ensemble. The form of  $\rho$  for other ensembles can be derived from the above two postulates.

## Connection to Thermodynamics

### Gibbs Entropy Formula

The Gibbs Entropy formula relates the entropy of a system to the probability distribution of the microstates. It can be derived from the above two postulates. Here we present it without proof.

$$S = -k_B \sum_{\nu} \text{Pr}(\nu) \ln[\text{Pr}(\nu)]$$

where  $\text{Pr}(\nu)$  is the probability of finding the system in the microstate  $\nu$  and  $k_B$  is the Boltzmann's constant.

### Microcanonical Ensemble

Consider an isolated system with  $N$  particles occupying a volume  $V$  with total energy having a value of  $E$ . Let  $\Omega$  be the number of microstates corresponding to this system.  $\Omega$  is also called the partition function of the microcanonical ensemble. From the Gibbs entropy formula, we can relate the partition function to entropy as follows

$$\begin{aligned} \text{Pr}(\nu) &= \frac{1}{\Omega} \\ S &= -k_B \sum_{\nu=1}^{\Omega} \frac{1}{\Omega} \ln\left(\frac{1}{\Omega}\right) = k_B \ln(\Omega) \\ \frac{1}{T} &= \left(\frac{\partial S}{\partial E}\right)_{N,V} = k_B \left(\frac{\partial \ln \Omega}{\partial E}\right)_{N,V} \\ \frac{\mu}{T} &= -\left(\frac{\partial S}{\partial N}\right)_{E,V} = -k_B \left(\frac{\partial \ln \Omega}{\partial N}\right)_{E,V} \\ \frac{P}{T} &= \left(\frac{\partial S}{\partial V}\right)_{N,E} = k_B \left(\frac{\partial \ln \Omega}{\partial V}\right)_{N,E} \end{aligned}$$

### Entropy of an ideal gas

In order to obtain the entropy of an ideal gas, we consider  $N$  non-interacting particles in a box and solve for the wave function using the Schrodinger equation. In the classical limit, the microcanonical partition function is given as

$$\Omega(N, V, E) = \frac{1}{h^{3N} N!} \int \dots \int d\mathbf{p}_1 \dots d\mathbf{p}_N d\mathbf{r}_1 \dots d\mathbf{r}_N \quad \text{such that } \sum_{i=1}^N \frac{|\mathbf{p}_i|^2}{2m} = E$$

$$= \frac{V^N}{h^{3N} N!} \frac{(2\pi m E)^{3N/2}}{(3N/2)!}$$

In the above equations  $h$  is the Planck's constant and  $N!$  indicates that all the particles are identical and hence indistinguishable. From the above equation, we can obtain expressions for various thermodynamics quantities as follows

$$S = k_B \ln \Omega$$

$$= Nk_B \left[ \frac{5}{2} + \ln \left( \frac{V}{N} \right) + \frac{3}{2} \ln \left( \frac{2E}{3N} \right) + \ln \left( \frac{(2\pi m E)^{3/2}}{h^3} \right) \right]$$

$$\frac{P}{T} = \left( \frac{\partial S}{\partial V} \right)_{E, N} = \frac{Nk_B}{V} \Rightarrow PV = Nk_B T$$

$$\frac{\mu}{T} = - \left( \frac{\partial S}{\partial N} \right)_{E, V} = \ln \left( \frac{h^3}{(2\pi m k_B T)^{3/2}} \right) + \ln P$$

$$\mu = \mu^0(T) + k_B T \ln P$$

In deriving the above equations we used the Stirling's formula for large  $N$

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

### Canonical Ensemble

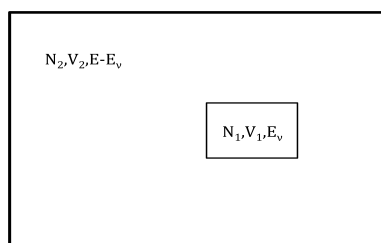


Figure 2: A closed system with surroundings isolated from the universe. The total energy of the system plus surroundings is  $E$ .

Consider a closed system with  $N_1$  particles occupying a volume  $V_1$  interacting with surroundings containing  $N_2$  particles and having volume  $V_2$ . We initially let the system plus surroundings interact with a heat bath having a temperature  $T$ . Once equilibrium is reached, both the system and the surroundings are removed from the heat bath and insulated. They now form an isolated system having a total energy  $E$ . During the interaction, the system can have different

energies corresponding to various microstates. Let  $E_\nu$  be the energy of the system corresponding to the microstate  $\nu$ . Due to conservation of energy, the surroundings will have energy  $E - E_\nu$ . The number of microstates possible for the surroundings is equal to  $\Omega(E - E_\nu)$ . Since the system plus the surroundings form an isolated system, from the postulate of equal *a-priori* probability we have

$$\Pr(\nu) \propto \Omega(E - E_\nu)$$

where  $\Pr(\nu)$  is the probability of finding the system in state  $\nu$ . If the surroundings are much larger than the system,  $E \gg E_\nu$ , and we can expand  $\Omega(E - E_\nu)$  in a Taylor series.

$$\ln[\Omega(E - E_\nu)] = \ln[\Omega(E)] - E_\nu \frac{\partial \ln \Omega}{\partial E} + \dots$$

$$= \ln[\Omega(E)] - \frac{E_\nu}{k_B T} + \dots$$

$$\Omega(E - E_\nu) \approx \Omega(E) \exp\left(-\frac{E_\nu}{k_B T}\right)$$

$$\Pr(\nu) \propto \exp\left(-\frac{E_\nu}{k_B T}\right)$$

$$\Pr(\nu) = \frac{\exp(-E_\nu / k_B T)}{\sum_\nu \exp(-E_\nu / k_B T)}$$

$$Q(N, V, T) = \sum_\nu \exp(-E_\nu / k_B T)$$

In the above equation,  $Q(N, V, T)$  is known as the partition function of the canonical ensemble. Since  $E_\nu$  has a degeneracy  $\Omega(E_\nu)$

$$Q(N, V, T) = \sum_E \Omega(E) \exp(-E / k_B T)$$

Through the application of the Gibbs entropy formula we can relate the partition function  $Q$  to the Helmholtz free energy  $A(N, V, T)$  as follows

$$\ln(\Pr) = -\frac{E_\nu}{k_B T} - \ln(Q)$$

$$S = -k_B \sum_\nu \Pr \left( -\frac{E_\nu}{k_B T} - \ln(Q) \right)$$

$$= \frac{\sum_\nu \Pr E_\nu}{T} + k_B \ln(Q) \sum_\nu \Pr$$

$$= \frac{\langle E \rangle}{T} + k_B \ln(Q)$$

$$-k_B T \ln(Q) = \langle E \rangle - TS = A(N, V, T)$$

In the classical limit, the canonical partition function for a system of  $N$  particles is given as

$$Q(N, V, T) = \frac{1}{\Lambda^{3N} N!} \int \dots \int \exp[-H(\mathbf{p}^N, \mathbf{r}^N)/k_B T] d\mathbf{p}^N d\mathbf{r}^N$$

where  $\Lambda$  is the thermal de-Broglie wavelength of the particle and is given as

$$\Lambda = \left( \frac{h^2}{2\pi m k_B T} \right)^{1/2}$$

$H(\mathbf{p}^N, \mathbf{r}^N) = \sum \frac{|\mathbf{p}|^2}{2m} + U(\mathbf{r}^N)$  is the Hamiltonian of the system. The first and the second terms denote the kinetic and potential energies of the particles respectively. For an ideal gas, the canonical partition function can be evaluated exactly and is given by

$$Q^{ig}(N, V, T) = \frac{V^N}{\Lambda^{3N} N!}$$

The rest of the thermodynamic properties can be derived from the partition function as follows.

$$A^{ig}(N, V, T) = -k_B T \ln Q = N k_B T [\ln(N \Lambda^3 / V) - 1]$$

$$P^{ig} = - \left( \frac{\partial A}{\partial V} \right)_{N, T} = \frac{N k_B T}{V}$$

$$U^{ig} = \left( \frac{\partial (A/T)}{\partial (1/T)} \right)_{N, V} = \frac{3}{2} N k_B T$$

$$C_V^{ig} = \left( \frac{\partial U}{\partial T} \right)_{N, V} = \frac{3}{2} N k_B$$

$$\begin{aligned} \mu^{ig} &= \left( \frac{\partial A}{\partial N} \right)_{V, T} = k_B T \ln(N \Lambda^3 / V) \\ &= k_B T \ln(\Lambda^3 / k_B T) + k_B T \ln P \\ &= \mu^0(T) + k_B T \ln P \end{aligned}$$

The ensemble averages in the canonical ensemble for a mechanical property,  $M$ , is calculated as follows

$$\langle M \rangle = \frac{\sum_v M_v \exp(-E_v / k_B T)}{Q(N, V, T)}$$

In the classical limit, the above equation becomes

$$\langle M \rangle = \frac{1}{\Lambda^{3N} N!} \frac{\int \dots \int M(\mathbf{p}^N, \mathbf{r}^N) \exp[-H(\mathbf{p}^N, \mathbf{r}^N)/k_B T] d\mathbf{p}^N d\mathbf{r}^N}{Q(N, V, T)}$$

## Grand Canonical Ensemble

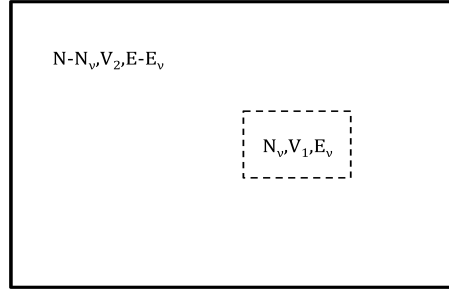


Figure 3: An open system with surroundings isolated from the universe containing a total of  $N$  particles. The total energy of the system plus surroundings is  $E$ .

Consider an open system with volume  $V_1$  interacting with a surrounding of volume  $V_2$ . Let the total number of particles in the system plus surrounding be equal to  $N$ . Initially the system plus surrounding are in contact with a large heat bath till equilibrium is attained. Then they are removed from the heat bath and isolated. Let  $E$  be the total energy of the system plus surroundings and  $T$  be their temperature. Let  $N_v$  and  $E_v$  be the number of particles and the energy of the system respectively for the microstate  $v$ . Hence the surroundings will contain  $N - N_v$  particles and have energy  $E - E_v$ . From the postulate of equal *a-priori* probability we have

$$\Pr(v) \propto \Omega(E - E_v, N - N_v)$$

If the surroundings are much larger than the system then we can expand  $\Omega(E - E_v, N - N_v)$  in a Taylor series as follows

$$\begin{aligned} \ln[\Omega(E - E_v, N - N_v)] &= \ln[\Omega(E, N)] - E_v \left( \frac{\partial \ln \Omega}{\partial E} \right)_{N, V} - N_v \left( \frac{\partial \ln \Omega}{\partial N} \right)_{E, V} + \dots \\ &= \ln[\Omega(E, N)] - \frac{E_v}{k_B T} + \frac{\mu N_v}{k_B T} + \dots \end{aligned}$$

$$\Omega(E - E_v, N - N_v) \approx \Omega(E, N) \exp\left(-\frac{E_v}{k_B T}\right) \exp\left(\frac{\mu N_v}{k_B T}\right)$$

$$\Pr(v) \propto \exp\left(-\frac{E_v}{k_B T}\right) \exp\left(\frac{\mu N_v}{k_B T}\right)$$

$$\Pr(v) = \frac{\exp(-E_v / k_B T) \exp(\mu N_v / k_B T)}{\sum_v \exp(-E_v / k_B T) \exp(\mu N_v / k_B T)}$$

$$\Xi(\mu, V, T) = \sum_v \exp(-E_v / k_B T) \exp(\mu N_v / k_B T)$$

In the above equation,  $\Xi(\mu, V, T)$  is known as the partition function of the grand canonical ensemble. Since  $E_v$  has a degeneracy  $\Omega(E_v)$

$$\Xi(\mu, V, T) = \sum_{N=0}^{\infty} \exp(\mu N / k_B T) \sum_E \Omega(E, N) \exp(-E / k_B T)$$

$\Xi(\mu, V, T)$  is related to the thermodynamic quantities as follows

$$PV = k_B T \ln(\Xi)$$

The classical form of the partition function is given as

$$\Xi(\mu, V, T) = \sum_{N=0}^{\infty} \frac{\exp(N\mu/k_B T)}{h^{3N} N!} \int \dots \int \exp(-H(\mathbf{p}^N, \mathbf{r}^N)) d\mathbf{p}^N d\mathbf{r}^N$$

The ensemble averages in the grand canonical ensemble for a mechanical property,  $M$ , is calculated as follows

$$\langle M \rangle = \frac{\sum_v M_v \exp(\mu N_v / k_B T) \exp(-E_v / k_B T)}{\Xi(\mu, V, T)}$$

In the classical limit, the above equation becomes

$$\langle M \rangle = \frac{1}{\Xi(\mu, V, T)} \sum_{N=0}^{\infty} \frac{\exp(\mu N / k_B T)}{\Lambda^{3N} N!} \int \dots \int M(\mathbf{p}^N, \mathbf{r}^N) \exp[-H(\mathbf{p}^N, \mathbf{r}^N) / k_B T] d\mathbf{p}^N d\mathbf{r}^N$$

## References

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