

# EP3120 - Statistical Physics and Applications

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## Abstract

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**Lecture Timings :** B Slot (Mon – 9am, Tue – 8am, Wed-1pm)

**Venue :** HSB 210

**Course Outline :** Some basic concepts in Probability Theory Microstates and macrostates; fundamental postulate of classical statistical mechanics; Thermal equilibrium; Microcanonical ensemble : Boltzmann's formula for Entropy; Laws of thermodynamics; Examples: Two-level systems, Classical ideal gas, Gibbs paradox Closed systems: canonical ensemble; Partition function, free energy; Calculation of thermodynamic quantities. Examples: Equation of state of a classical ideal gas; Energy fluctuations and specific heat. Open systems: grand canonical ensemble; Number fluctuations. Bosons, fermions and the elements of quantum statistics. Ideal fermi gas at absolute zero; application to electrons in metals and semiconductors. Electronic specific heat. Pauli paramagnetism. Blackbody radiation, derivation of Planck's Distribution Law. Radiation pressure. Elements of phase transition phenomena. First order and continuous phase transitions, critical point.

**Text books :**

M Kardar, Statistical Physics of Particles, Cambridge University Press (2007).

K.Huang, Statistical Mechanics (2nd Edition, Wiley, 1987).

**Pre-requisite:** PH 1080 - Thermodynamics and Kinetic Theory

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# Chapter 1

## Thermodynamics(Review)

### Lecture 1: First Lecture

#### 1.1 Preliminaries

25 July 2022

**Definition 1.1.1.** A *Thermodynamic system* is any macroscopic system.

**Definition 1.1.2.** *Thermodynamic Parameters* are measurable macroscopic quantities associated with the system, such as the pressure  $P$ , the volume  $V$ , the temperature  $T$ , and the magnetic field  $H$ . They are defined experimentally.

**Definition 1.1.3.** A *Thermodynamic state* is specified by a set of values of all the thermodynamic parameters necessary for the description of the system.

**Definition 1.1.4.** *Thermodynamic equilibrium* prevails when the thermodynamic system does not change with time.

**Definition 1.1.5.** The *equation of state* is a functional relationship among the thermodynamic parameters for a system in equilibrium. If  $P$ ,  $V$ , and  $T$  are the thermodynamic parameters of the system, the equation of state takes the form

$$f(P, V, T) = 0$$

which reduces the number of independent variables of the system from three to two. The function  $f$  is assumed to be given as part of the specification of the system. It is customary to represent the state of such a system by a point in the three-dimensional  $P$ - $V$ - $T$  space. The equation of state then defines a surface in this space, as shown in Fig.1.1. Any point lying on this surface represent a state in equilibrium. In thermodynamics a state is automatically means a state in equilibrium unless otherwise specified.

**Definition 1.1.6.** A *thermodynamic transformation* is a change of state. If the initial state is an equilibrium state, the transformation can be brought about only by changes in the external condition of the system. The transformation is quasi-static if the external condition changes so slowly that at any moment the system is approximately in equilibrium. It is reversible if the transformation retraces its history in time when the external condition retraces its history in time. A reversible transformation is quasi-static, but the converse is not necessarily true. For example, a gas that freely expands into successive infinitesimal volume elements undergoes a quasi-static transformation but not a reversible one.

**Definition 1.1.7.** The *P-V diagram* of a system is the projection of the surface of the equation of state onto the P-V plane. Every point on the P-V diagram therefore represents an equilibrium state. A reversible transformation is a continuous path on the P-V diagram. Reversible transformations of specific types give rise to paths with specific names, such as *isotherms*, *adiabatics*, etc. A transformation that is not reversible cannot be so represented.

**Definition 1.1.8.** The concept of *work* is taken over from mechanics. For example, for a system whose parameters are P, V, and T, the work  $dW$  done by a system in an infinitesimal transformation in which the volume increases by  $dV$  is given by

$$dW = PdV$$

**Definition 1.1.9.** *Heat* is what is absorbed by a homogeneous system if its temperature increases while no work is done. If  $\Delta Q$  is a small amount of the heat absorbed, and  $\Delta T$  is the small change in temperature accompanying the absorption of heat, the heat capacity  $C$  is defined by

$$\Delta Q = C\Delta T$$

The heat capacity depends on the detailed nature of the system and is given as a part of the specification of the system. It is an experimental fact that, for the same  $\Delta T$ ,  $\Delta Q$  is different for different ways of heating up the system. Correspondingly, the heat capacity depends on the manner of heating. Commonly considered heat capacities are  $C_v$  and  $C_p$  which respectively correspond to heating at constants V and P. Heat capacities per unit mass or per mole of a substance are called specific heats.

**Definition 1.1.10.** A *heat reservoir*, is a system so large that the gain or loss of any finite amount of heat does not change its temperature.

**Definition 1.1.11.** A system is *thermally isolated* if no heat exchange can take place between it and the external world. Thermal isolation may be achieved by surrounding a system with an adiabatic wall. Any transformation the system can undergo in thermal isolation is said to take place adiabatically.

**Definition 1.1.12.** A thermodynamic quantity is said to be *extensive* if it is proportional to the amount of substance in the system under consideration and is said to be *intensive* if it is independent of the amount of substance in the system under consideration. It is an important empirical fact that to a good approximation thermodynamic quantities are either extensive or intensive.

**Example.** *extensive*:- volume  $V$ , No. of molecules  $N$ . *intensive*:- pressure  $P$ , temperature  $T$ , specific density  $n = \frac{N}{V}$ , specific volume  $\vartheta = \frac{V}{N}$

**Definition 1.1.13.** The *ideal gas* is an important idealized thermodynamic system. Experimentally all gases behave in a universal way when they are sufficiently dilute. The ideal gas is an idealization of this limiting behavior. The parameters for an ideal gas are pressure  $P$ , volume  $V$ , temperature  $T$ , and number of molecules  $N$ . The equation of state is given by Boyle's law:

$$\frac{PV}{N} = \text{constant}$$

(for constant temperature)

The value of this constant depends on the experimental scale of temperature used.

**Definition 1.1.14.** The equation of state of an ideal gas in fact defines a temperature scale, The ideal-gas temperature  $T$ :

$$PV = Nk_bT$$

where

$$k_b = 1.38 \times 10^{-16} \frac{\text{erg}}{\text{deg}}$$

which is called Boltzmann's constant. Its value is determined by the conventional choice of temperature intervals, namely, the Centigrade degree. This scale has a universal character because the ideal gas has a universal character. The origin  $T = 0$  is here arbitrarily chosen. Later we see that it actually has an absolute meaning according to the second law of thermodynamics.

## Lecture 2: Second Lecture

### 1.2 Thermodynamic Laws

26 July 2022

#### 1.2.1 Zeroth Law

**Definition 1.2.1.** If A is in Thermodynamic equilibrium with B and B is in Thermodynamic equilibrium with C, then C is in thermodynamic equilibrium with A. This law defines the notion of temperature ( $T$ ).

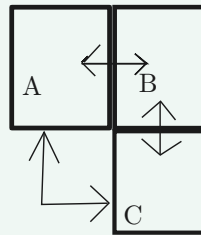


Figure 1.1: Zeroth Law

#### 1.2.2 First Law

##### Work Done

Conjugate variables

$P \rightarrow \Delta V$

$\mu(\text{Chemical Potential}) \rightarrow \Delta N$

$F \rightarrow \Delta L$

**Quasi-static process:**  $PdV$  = infinitesimal work done.

$$\Delta W = \int_A^B PdV$$

Since, Work done is path dependent it is inexact differential and written as  $d(\text{bar})W$  **Heat exchange** : It is also path dependent so, an inexact differential  $d(\text{bar})Q = SdT$

**Definition 1.2.2 (First Law).** There exists a quantity called "Internal Energy"

$$\Delta U = \Delta Q - \Delta W$$

$$dU = dQ - dW$$

$dU$  is an exact differential, depends only on initial and final states.  
It is an extensive quantity.

**Ideal gas:** State is defined by (P, V, T)

Equation of state is given by  $PV = Nk_bT$ . This is a constraint so, independent variables reduce to 2.

$$U(P, V) \Rightarrow dU = \left(\frac{\partial U}{\partial P}\right)_V dP + \left(\frac{\partial U}{\partial V}\right)_P dV$$

$$U(T, V) \Rightarrow dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

$$U(P, T) \Rightarrow dU = \left(\frac{\partial U}{\partial P}\right)_T dP + \left(\frac{\partial U}{\partial T}\right)_P dT$$

**Definition 1.2.3 (Specific Heat).**  $dQ = C_V dT$  or  $C_P dT$  response of the system to heat.

**Constant Volume Process:**

$$dU = dQ - PdV$$

we know for a constant volume process  $dQ = C_V dT$ ,

$$dU = C_V dT - PdV$$

we also know,

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

$\therefore V$  is constant  $\Rightarrow dV = 0$ .

Equating the above 2 equations gives,

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

**Constant Pressure process :**

we know,

$$dQ = C_P dT$$

$$dU = C_P dT - PdV$$

we also know,

$$dU = \left(\frac{\partial U}{\partial P}\right)_T dP + \left(\frac{\partial U}{\partial T}\right)_P dT$$

$dV$  term is there in the equation. Since,  $V$  is a function of  $P$  and  $T$  we can write,

$$dV = \left(\frac{\partial V}{\partial P}\right)_T dP + \left(\frac{\partial V}{\partial T}\right)_P dT$$

Substituting  $dV$  in first equation,

$$dU = C_P dT - P \left( \left(\frac{\partial V}{\partial P}\right)_T dP + \left(\frac{\partial V}{\partial T}\right)_P dT \right)$$

since, constant pressure  $dP = 0$ . Therefore,

$$C_P = P \left(\frac{\partial V}{\partial T}\right)_P + \left(\frac{\partial U}{\partial T}\right)_P$$

**Definition 1.2.4** (Enthalpy, H). Thermodynamic Potential, Enthalpy  $H = U + PV$

$$dH = dU + PdV$$

$$C_P = \left( \frac{\partial H}{\partial T} \right)_P$$

Heat Engine :  
Isothermal Process

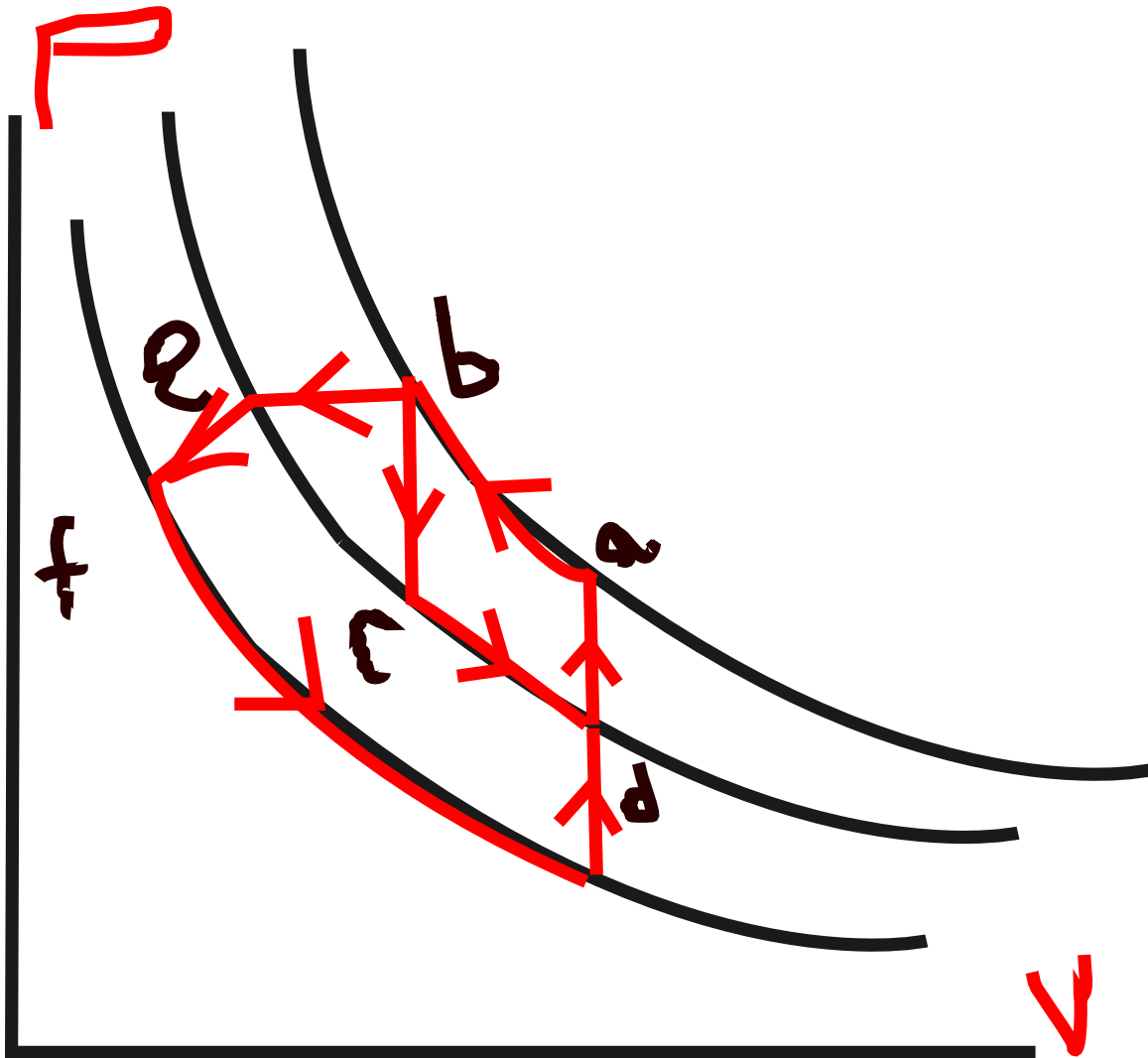


Figure 1.2: cyclic process

**Adiabatic Process** : Constant heat Process.

$$dQ = 0$$

$$dU = -dW$$

$$dU = -PdV$$



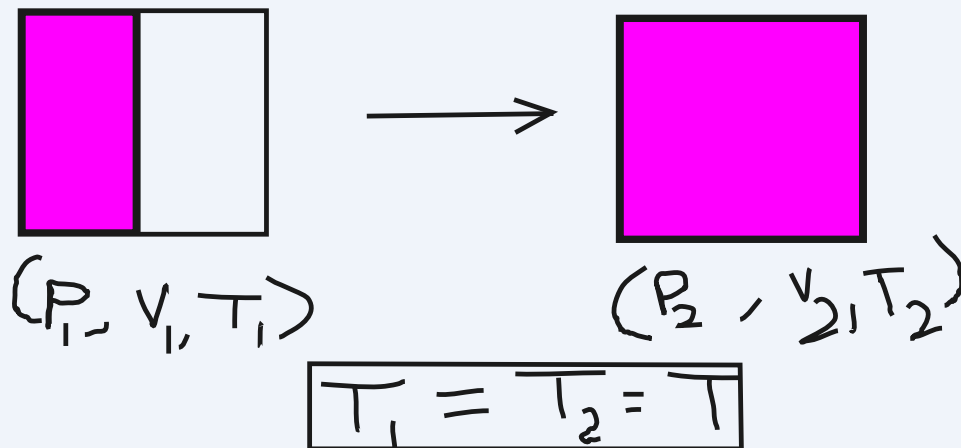


Figure 1.3: Free expansion

**Example** (Ideal Gas Adiabatic free expansion).

$$dQ = 0 \because \text{Adiabatic}$$

$$dW = 0 \because \text{FreeExpansion}$$

Since, Free expansion.

$$\therefore dU = 0 \rightarrow f(P, V) = 0$$

## Lecture 3: Third Lecture

$$dU = dQ - dW$$

27 July 2022

**Free expansion** Irreversible Process

$$\Delta W = 0, \Delta Q = 0 \Rightarrow \Delta U = 0$$

$$U(P, V, T) = U(V, T) (\because PV = Nk_B T)$$

$$\Rightarrow U(V_i, T) = U(V_f, T)$$

Internal energy is purely a function of T.

$$C_V = \left( \frac{\partial U}{\partial T} \right)_V = \frac{dU}{dT}$$

$$H = U + PV = U(T) + Nk_B T$$

$$\Rightarrow H = H(T)$$

$$\therefore C_P = \left( \frac{\partial H}{\partial T} \right)_P$$

$$\Rightarrow C_P = \frac{dU}{dT} + Nk_B$$

$$\Rightarrow C_P = C_V + Nk_B \Rightarrow \gamma = \frac{C_P}{C_V} > 1$$

**Adiabatic Process [Ideal Gas]:**

$$\begin{aligned}
dQ &= 0 \\
\Rightarrow dU &= dW = -PdV \\
C_V dT &= -PdV \\
C_V PdV + C_V V dP + PNk_B dV &= 0 (\because PdV + VdP = Nk_B dT) \\
\Rightarrow C_P PdV + C_V V dP &= 0 \\
\Rightarrow \gamma \frac{dV}{V} + \frac{dP}{P} &= 0 \\
\Rightarrow PV^\gamma &= \text{Constant}.
\end{aligned}$$

**Note.** In class a question is raised which is worth discussing.

**Exercise.** Ideal gas law  $\Rightarrow PV = \text{constant}$  for free expansion (Adiabatic Irreversible process.)  
 Adiabatic Process  $\Rightarrow PV^\gamma = \text{constant}$ .

$$P_1 V_1 = P_2 V_2$$

$$P_1 V_1^\gamma = P_2 V_2^\gamma$$

dividing both equations gives...

$$V_1^{\gamma-1} = V_2^{\gamma-1} \Rightarrow V_1 = V_2$$

But the process is free **expansion**. Can you explain why?

**Answer.** We obtained  $PV^\gamma = \text{constant}$  equation by taking  $dW = -PdV$  which means the process is reversible.

Where as the free expansion process is Irreversible so, we cannot use  $PV^\gamma = \text{constant}$  for this process. ⊗

**1.2.3 Second Law**

- Definition 1.2.5 (Second Law).**
1. The sole amount of a cyclic process cannot be the conversion of heat to work.
  2. (corollary) Efficiency of a carnot engine  $\neq 1$ .
  3. It is not possible to have a cyclic process whose sole outcome is transfer of heat from cooler bath to a heater bath.

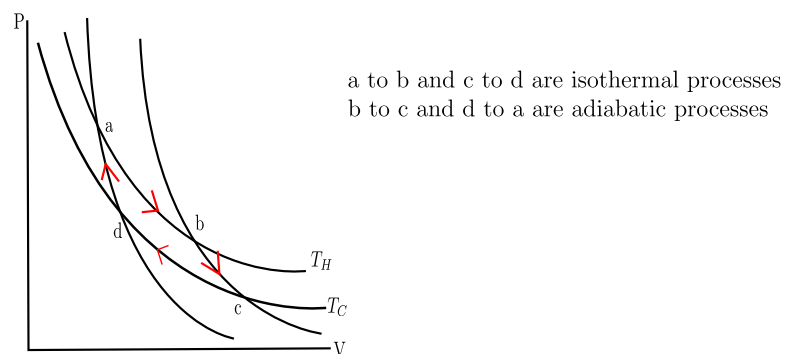


Figure 1.4: carnot cycle

Efficiency of the carnot engine

$$\eta = \frac{W}{Q_H} = \frac{Q_H - Q_C}{Q_H} = 1 - \frac{Q_C}{Q_H} \quad (1.1)$$

We should do work to dump heat from cooler reservoir to hotter reservoir.

**Reverse Carnot cycle  $\Rightarrow$  Refrigerator.**

## Entropy

**Proposition 1.2.1 (Clausius Theorem).**

$$\oint_{\text{cyclic process}} \frac{dQ}{T} \leq 0 \text{ with equality holding iff the process is reversible.} \quad (1.2)$$

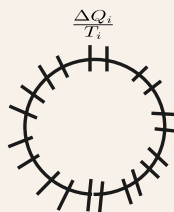


Figure 1.5: cyclic process

**Definition 1.2.6 (Entropy). Reversible Process**

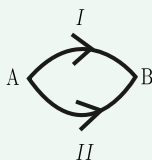


Figure 1.6: reversible process

$$\oint \frac{dQ}{T} = 0 \quad (1.3)$$

$$\oint \frac{dQ}{T} - \oint_{II} \frac{dQ}{T} = 0 \quad (1.4)$$

$$\oint_I \frac{dQ}{T} = \oint_{II} \frac{dQ}{T} \Rightarrow S(B) - S(A) \text{ where, } S = \text{entropy.} \quad (1.5)$$

**Absolute notion of entropy**

$$\int_0^A \frac{dQ}{T} = S(A) - S(0) \Rightarrow dQ = TdS (\because S(0) = 0) \quad (1.6)$$

### 1.2.4 Third Law of Thermodynamics

**Definition 1.2.7.** Impossible to attain 0K.  $S(\text{"Absolute zero"}) = 0$

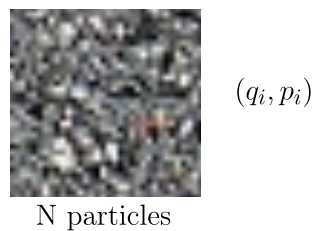
# Chapter 2

## Statistical mechanics

### 2.1 Microstates

In a **Macrostate** Pressure(P), Volume(V), Temperature(T), Number of particles(N) are thermodynamic variables and Internal energy (U), Enthalpy (H), Entropy (S) are functions of thermodynamic variables.

In a **Microstate**, Number of particles are  $O(10^{23})$ , Volume  $\approx 10^{23}$  molar volume.  $\frac{N}{V} = n$ , number density in "thermodynamic limit"  $N \rightarrow \infty, V \rightarrow \infty, n = \text{Constant}$ .



$$H = KE + PE = H(\{p_i, q_i\}_{i=1,2,\dots,3N})$$

Figure 2.1

Hamiltonian,  $H \in [E, E + dE]$  is a constraint for Thermal Equilibrium.

#### Phase space

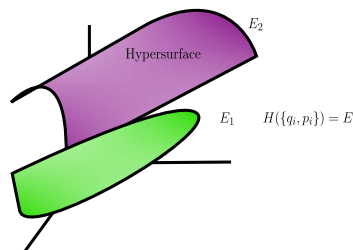


Figure 2.2: phase space

different  $\{q_i, p_i\}$  may give same E each  $\{q_i, p_i\}$  is a microstate. Microstate  $\equiv (q_1, q_2, \dots, q_N, p_1, p_2, \dots, p_N)$   
 Several microstates, ("Ensemble")("collection")  $\Rightarrow$  E(total energy).

What are the Probabilities??

**Microcanonical Ensemble:** All microstates are equally likely, so long as they give total energy  $\in$

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$[E, E + dE]$ .

**Canonical Ensemble:** Probabilities are not equal. **Gibbs Canonical Ensemble:** Number of particles change.

## Lecture 4: Fourth Lecture

### Statistical point of view

01 August 2022

Can we derive **equilibrium properties** of macroscopic systems from the **statistical properties** of the microscopic parts. **Microstate:**  $(q_1, q_2, \dots, q_N, p_1, p_2, \dots, p_N)$   $N$  particles. Probabilities of microstates, subject to **external constraints** (equilibrium condition)

- Eugene wigner; "unreasonable effectiveness of mathematics in the physical sciences."
- Wigner semi-circle distribution. (See tutorial 1 for more information.)

## 2.2 Review of probability theory

Random Variable:  $x$  (discrete, continuous)

## Chapter 3

# Canonical Ensemble

### Lecture 17

05 sep 2022

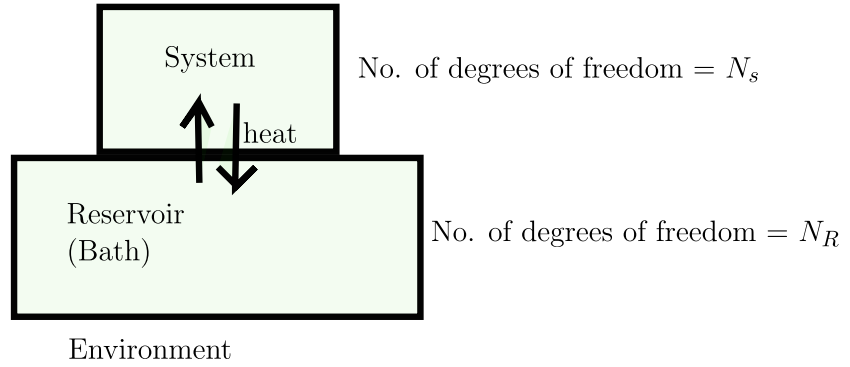


Figure 3.1: title

System + Reservoir  $\rightarrow$  isolated system  
Microcanonical Ensemble

$$H_s(\{\vec{p}_s, \vec{q}_s\}) \quad \{\vec{p}_s, \vec{q}_s\} = \text{gen. coordinates for system}$$

$$H_R(\{\vec{p}_R, \vec{q}_R\}) \quad \{\vec{p}_R, \vec{q}_R\} = \text{gen. coordinates for reservoir}$$

$$H_{tot} = H_s + H_R = E_{tot} = E_R + E_s \gg E_s \Rightarrow E_{tot} = E_{tot} \approx E_R$$

$$\text{Joint p.d.f} \rightarrow p_{TVNM}(\{\vec{p}_s, \vec{q}_s, \vec{p}_R, \vec{q}_R\}) = \frac{1}{\Omega_{s \oplus R}(E_{tot}, N, V)} \begin{cases} 1, & \text{when } H_s + H_R = E_{tot}; \\ 0, & \text{otherwise.} \end{cases}$$

$$\text{Marginal p.d.f} p_{TVN}(\{\vec{p}_s, \vec{q}_s\}) = \sum_{\{\vec{p}_R, \vec{q}_R\}} p_{TVNM}(\{\vec{p}_s, \vec{q}_s, \vec{p}_R, \vec{q}_R\}) = \int d\vec{p}_R d\vec{q}_R p_{TVNM}(\{\vec{p}_s, \vec{q}_s, \vec{p}_R, \vec{q}_R\})$$

$$H_s(\{\vec{p}_s, \vec{q}_s\}) = E_{tot} = H(\{\vec{p}_R, \vec{q}_R\})$$

$$p_{TVN}(\{\vec{p}_s, \vec{q}_s\}) = \frac{\Omega_R[E_{tot} - H_s(\{\vec{p}_s, \vec{q}_s\})]}{\Omega_{R \oplus s}(E_R + E_s)}$$

$$\approx \frac{e^{\frac{1}{k_B} S_R[E_{tot} - H_s(\{\vec{p}_s, \vec{q}_s\})]}}{e^{\frac{1}{k_B} S_R(E_R)}} \quad (\because S_{tot} = k_B \Omega_{tot}(E_s + E_R) \text{ and } S_R = k_B \Omega_R(E_R))$$

$$p_{TV}(\{\vec{p}_s, \vec{q}_s\}) \approx \frac{e^{\frac{1}{k_B}[S_R(E_R) - (\frac{\partial S}{\partial E})_V H_s(\{\vec{p}_s, \vec{q}_s\})]}}{e^{\frac{1}{k_B}[S_R(E_R)]}} \approx e^{-\frac{1}{k_B T}[H_s(\{\vec{p}_s, \vec{q}_s\})]} \quad (\because E_{tot} \gg H_s(\{\vec{p}_s, \vec{q}_s\}) \forall \{\vec{p}_s, \vec{q}_s\} \text{ and } \beta = \frac{1}{k_B T})$$

Phase space distribution

$$p_{TVN}(\{\vec{p}_s, \vec{q}_s\}) = \frac{1}{Z(T)} [e^{-\beta H_s(\{\vec{p}_s, \vec{q}_s\})}]$$

Normalize:

$$\sum_{\{\vec{p}_s, \vec{q}_s\}} p_{TV}(\{\vec{p}_s, \vec{q}_s\}) = 1 \quad \text{Canonical Ensemble}$$

**Partition Function**

$$Z(T) = \sum_{\{\vec{p}_s, \vec{q}_s\}} e^{-\beta H_s(\{\vec{p}_s, \vec{q}_s\})} = \int d\vec{p}_s d\vec{q}_s e^{-\beta H_s(\{\vec{p}_s, \vec{q}_s\})}$$

**Internal energy**  $E_s$  is a random variable  $\equiv \epsilon$

$$\begin{aligned} p_{TV}(\epsilon) &= \sum_{\{\vec{p}_s, \vec{q}_s\}} p(\{\vec{p}_s, \vec{q}_s\}) \delta(H_s(\{\vec{p}_s, \vec{q}_s\}) - \epsilon) \\ &= \frac{1}{Z(T)} e^{\frac{\beta}{\epsilon}} \int_{H_s(\{\vec{p}_s, \vec{q}_s\})=\epsilon} d\vec{p}_s d\vec{q}_s \\ \int_{H_s(\{\vec{p}_s, \vec{q}_s\})=\epsilon} d\vec{p}_s d\vec{q}_s &\text{ is Number of microstates corresponding to energy } \epsilon \\ p_{TV}(\epsilon) &= \frac{e^{\frac{\beta}{\epsilon}}}{Z(T)} [\Omega_s(\epsilon)] \\ &= \frac{e^{-\frac{\epsilon}{k_B T}} e^{\frac{1}{k_B} S(\epsilon)}}{Z(T)} = \frac{e^{-\frac{1}{k_B T}(\epsilon - TS)}}{Z(T)} \end{aligned}$$

**Definition 3.0.1.** Helmholtz free energy  $\Rightarrow$  Thermodynamic "Potentials"

$$F = \epsilon - TS$$

$$p_{TV}(\epsilon) = \frac{e^{-\beta F(\epsilon)}}{Z(T)} \rightarrow \text{Normalized ?}$$

$$Z(T) = \sum_{\epsilon} e^{-\beta F(\epsilon)} = \sum_{\{\vec{p}_s, \vec{q}_s\}} e^{-\beta H_s}$$

Most Probable value of energy ?  $\Rightarrow F(\epsilon)$  is minimized !  $\epsilon^*$  that minimizes  $F(\epsilon) = \epsilon - TS$  (potential)

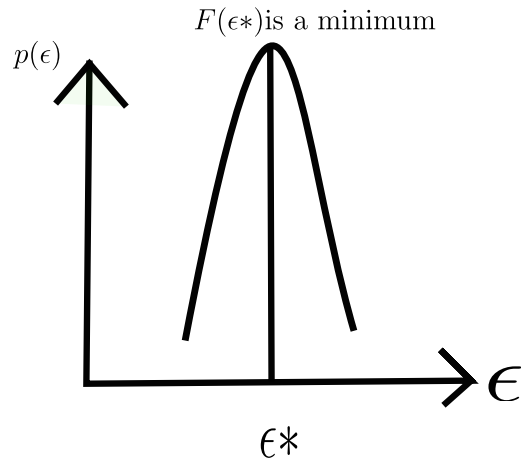


Figure 3.2: title



## Average Energy

$$\langle H_s \rangle = \sum_{\{\vec{p}_s, \vec{q}_s\}} p_{TV}(\{\vec{p}_s, \vec{q}_s\}) H_s(\{\vec{p}_s, \vec{q}_s\}) = \frac{1}{Z(T)} \sum_{\{\vec{p}_s, \vec{q}_s\}} e^{-\beta H_s} H_s$$

$$\langle H_s \rangle = \frac{1}{Z(T)} \left( -\frac{\partial Z(T)}{\partial \beta} \right)$$

$$\boxed{\langle H_s \rangle = -\frac{\partial \ln Z(T)}{\partial \beta}}$$

$$H_s(\{\vec{p}_s, \vec{q}_s\}) \rightarrow \text{random variable} \quad (3.1)$$

$$Z(T) \text{ is like a characteristic function } (ik \equiv \beta) \quad (3.2)$$

$$\ln(Z) \text{ generates cummulants!} \quad (3.3)$$

## Lecture 18: Canonical Ensemble - II

## Partition function

06 sep 2022

$$Z(T) = \sum_{\{\vec{p}_s, \vec{q}_s\}} e^{-\beta H_s(\{\vec{p}_s, \vec{q}_s\})} = \frac{1}{h^{3N}} \int_{\{\vec{p}_s, \vec{q}_s\}} d\vec{p}_s d\vec{q}_s e^{-\beta H_s(\{\vec{p}_s, \vec{q}_s\})}$$

## Internal Energy

$$p(\epsilon) = \frac{e^{-\beta(\epsilon - TS(\epsilon))}}{Z(T)} = \frac{e^{-\beta F(\epsilon)}}{Z(T)}$$

$$\text{Helmholtz energy } F = \epsilon - TS$$

$$\text{Internal Energy } U = F + TS$$

$$\text{Most Probable energy } \epsilon^* : \text{ minimizes } F(\epsilon)$$

Recall,

$$U = F + TS$$

$$dU = dF + TdS + SdT$$

$$S = - \left( \frac{\partial F}{\partial T} \right)_{V, N}$$

 $\epsilon^* \equiv$  most Probable energy.

$$Z(T) = \sum_{\{\vec{p}_s, \vec{q}_s\}} e^{-\beta H_s(\{\vec{p}_s, \vec{q}_s\})} = \sum_{\{\epsilon\}} e^{-\beta F(\epsilon)} \approx e^{-\beta F(\epsilon^*)} (\cdot: \text{dominant term})$$

$$F(\epsilon^*) = -k_B T \ln Z$$

$$\epsilon^* \approx \langle H_s \rangle \text{ ( average energy )} = U \rightarrow \text{ ( At equilibrium ) } F = -k_B T \ln Z$$

$$\langle H_s \rangle = \sum_{\{\vec{p}_s, \vec{q}_s\}} \frac{e^{-\beta H_s(\{\vec{p}_s, \vec{q}_s\})}}{Z(T)} H_s(\{\vec{p}_s, \vec{q}_s\}) = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = -\frac{\partial \ln Z}{\partial \beta}$$

$$\beta \Leftrightarrow ik \begin{cases} \ln Z \equiv \text{ cummulant generating function} \\ Z \equiv \text{ Characteristic function} \end{cases}$$

$$\langle H_s^2 \rangle = \sum_{\{\vec{p}_s, \vec{q}_s\}} H_s^2 \frac{e^{-\beta H_s}}{Z(T)} = \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2}$$

variance of energy

$$\Delta^2 H_s = \langle H_s^2 \rangle - \langle H_s \rangle^2 \equiv \langle H_s^2 \rangle_c \text{ ( 2nd cummulants )}$$

$$\Delta^2 H_s = \frac{1}{Z} \frac{\partial Z}{\partial \beta^2} - \frac{1}{Z^2} \left( \frac{\partial Z}{\partial \beta} \right)^2 = \frac{\partial}{\partial \beta} \left( \frac{1}{Z} \frac{\partial Z}{\partial \beta} \right)$$

$$\Delta^2 H_s = \frac{\partial \langle H_s \rangle}{\partial \beta} \quad (\because \langle H_s \rangle = \frac{1}{Z} \frac{\partial Z}{\partial \beta})$$

$$\Delta^2 H_s = k_B T^2 \left( \frac{\partial \langle H_s \rangle}{\partial T} \right) = k_B T^2 \left( \frac{\partial U}{\partial T} \right)_{N,V} \quad (\because \beta = \frac{1}{k_B T} \Rightarrow d\beta = -\frac{1}{k_B T^2} dT)$$

$$\Delta^2 H_s = k_B T^2 C_V$$

$$C_V \approx O(N); \quad \text{fluctuations} = \frac{\text{std. deviation}}{\langle H_s \rangle} = \frac{\sqrt{k_B T^2 C_V}}{\langle H_s \rangle} \approx \frac{\sqrt{N}}{N} \approx \frac{1}{\sqrt{N}} \rightarrow 0 \text{ as } N \rightarrow \infty$$

figure

$$\langle H_s \rangle = -\frac{\partial \ln Z}{\partial \beta}$$

$$U = F + TS = F - T \left( \frac{\partial F}{\partial T} \right)_{N,V} = F - \beta \frac{\partial F}{\partial \beta} = \frac{\partial(\beta F)}{\partial \beta}$$

from above 2 equations  $\Rightarrow \boxed{F = -k_B T \ln Z}$  average internal energy

Recall, for a Microcanonical Ensemble,

$$S = k_B \ln \Omega \text{ Boltzmann}$$

$$- \sum_{\{\vec{p}_s, \vec{q}\}} p_E(\{\vec{p}_s, \vec{q}\}) \ln p_E(\{\vec{p}_s, \vec{q}\}) \text{ Shannon definition}$$

For a uniform distribution,  $p_E(\{\vec{p}_s, \vec{q}\}) = \frac{1}{\Omega} \forall \{\vec{p}_s, \vec{q}\}$

$$\text{Shannon Entropy, } S = k_B \Omega \left( \frac{1}{\Omega} \ln \Omega \right) = k_B \ln \Omega$$

Shannon entropy is same as Boltzmann entropy.

## Lecture 19: Canonical ensemble-III

$$p_{T,V} = \frac{e^{-\beta H_s(\{\vec{p}_s, \vec{q}_s\})}}{Z(T)} ; ; Z(T) = \sum_{\{\vec{p}_s, \vec{q}_s\}} e^{-\beta H_s(\{\vec{p}_s, \vec{q}_s\})}$$

$$F = -k_B T \ln Z = U - TS$$

$$S = -k_B \sum_{\{\vec{p}_s, \vec{q}_s\}} p_{T,N}(\{\vec{p}_s, \vec{q}_s\}) \ln p_{T,N}(\{\vec{p}_s, \vec{q}_s\})$$

$$S = -k_B \langle \ln p_{T,V}(\{\vec{p}_s, \vec{q}_s\}) \rangle$$

$$\ln(p_{T,V}(\{\vec{p}_s, \vec{q}_s\})) = -\beta H(\{\vec{p}_s, \vec{q}_s\}) - \ln Z$$

$$\Rightarrow S = k_B \beta \langle H \rangle + k_B \langle \ln Z \rangle = \frac{\langle H \rangle}{T} + \langle k_B \ln Z \rangle$$

$$S = \frac{U}{T} + \frac{\langle F \rangle}{T} \Rightarrow TS = U - F$$

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### 3.1 Two-level system

Occupation number  $n_i = \{0, 1\}$

Random variables  $\equiv n_i, i = 1, 2, 3 \dots N$  (state space)

At equilibrium with a bath at temperature  $T$ .

Total energy  $E = \sum_i n_i \epsilon = \epsilon N_1$  where  $N_1$  of system of particles in the excited state.

**Process**

1. Find partition function first.  $Z(T)$

**partition function**

$$Z(T) = \sum_{n_i} e^{-\beta H} = \sum_{n_i} e^{-\beta \sum_i n_i \epsilon}$$

$$Z(T) = \sum_{\{n_i\}} \prod_i e^{-\beta n_i \epsilon} = \prod_{i=1}^N \sum_{n_i=0}^1 e^{-\beta n_i \epsilon} = \prod_{i=1}^N (1 + e^{-\beta \epsilon}) = (1 + e^{-\beta \epsilon})^N$$

$$Z(T) = (1 + e^{-\beta \epsilon})^N$$

$$F(T, N) = -k_B T N \ln[1 + e^{-\beta \epsilon}]$$

$$S = - \left( \frac{\partial F}{\partial T} \right)_N = N k_B \ln[1 + e^{-\beta \epsilon}] + \frac{N \epsilon e^{-\beta \epsilon}}{T(1 + e^{-\beta \epsilon})}$$

$$S = - \frac{F}{T} + \frac{N \epsilon e^{-\beta \epsilon}}{T(1 + e^{-\beta \epsilon})}$$

$$U = F + TS = \frac{N \epsilon e^{-\beta \epsilon}}{T(1 + e^{-\beta \epsilon})}$$

$$p_{T,N}(\{n_i\}) = \frac{e^{-\beta \sum_i n_i \epsilon}}{Z} = \frac{\prod_i e^{-\beta n_i \epsilon}}{(1 + e^{-\beta \epsilon})^N}$$

Distribution of a given composition  $n_i =$  marginal of  $p(\{n + i\}) = \frac{e^{-\beta n_i \epsilon}}{1 + e^{-\beta \epsilon}}$ .

### 3.2 Ideal Gas

1.  $N$  particles in vol  $V$  at temp  $T$  (non - interacting)

2. Macrostate  $\equiv (T, V, N)$

3. Microstate  $\equiv \{p_i, q_i; i = 1, 2 \dots 3N\}$

4.  $H = \sum_{i=1}^{3N} \frac{p_i^2}{2m}$

**Partition function**

$$Z(T) = \frac{1}{h^{3N} N!} \int d\vec{p} d\vec{q} (e^{-\beta H})$$

$$Z(T) = \frac{1}{h^{3N} N!} \int d\vec{p} d\vec{q} e^{-\beta (\sum_i \frac{p_i^2}{2m})}$$

$$Z(T) = \frac{1}{h^{3N} N!} \int d\vec{p} \int d\vec{q} \prod_i^N e^{-\beta \frac{p_i^2}{2m}}$$

$$Z(T) = \frac{V^N}{h^{3N} N!}$$

# Appendix