State of the system in Equilibrium

- Macroscopic state
  - Macroscopic Variables
- Microscopic state
  - Microscopic Variables

Microscopic Variables

- Generalized Coordinates
  \( q_1, \ldots, q_n \)
- Generalized Momenta
  \( p_1, \ldots, p_n \)
Variables

- Mechanical Variables: \( p, E, V, N \)
- Nonmechanical Variables: \( T, S, F, G \)

Equilibrium and Measured values of Macroscopic Variables

\[ F_{measured} = \frac{1}{\tau} \int_{t_0}^{t_0+\tau} f(p(t), q(t)) dt \]

Ensemble

is a mental collection of a large number of macroscopic systems, each of which is a duplicate, on macroscopic scale, of the system whose properties we are trying to deduce.
Ensemble

- Some properties are held constant for each member of the ensemble
- Some properties may vary from member to member

Types of Ensembles

- Microcanonical ensemble
  \( N, V, E \)
- Canonical ensemble
  \( N, V, T \)
- Grand canonical ensemble
  \( \mu, V, T \)

Probability density (Distribution Function)

\[
p(p, q, t),
\]

\[
\int p(p, q, t) \, dp \, dq = 1
\]
Ensemble Average

\[ f(p, q), \]

\[ \bar{F} = \int f(p, q) p(p, q, t) dp dq \]

Postulates

- For an insulated system, having constant N, V, and E, all accessible microstates of the system, which necessarily have the same energy, are equally probable.
- For any ensemble, the long-time average of any mechanical property of the real system on which the ensemble is based is equal to the properly weighted mean of that property taken over the appropriate ensemble.

Microcanonical Ensemble

- Closed Isolated System in Equilibrium

\[ p = \text{const}, \quad H(p, q) = E \quad \text{to} \quad E + \delta E, \]

\[ p = 0, \quad \text{otherwise} \]
Microcanonical Ensemble

$$\bar{F} = \frac{1}{\tau} \int_0^\tau f(p,q) \, ds =$$

$$= \int_{E \leq H(p,q) \leq E + \delta E} f(p,q) \, d\mathbf{p} d\mathbf{q}$$

$$= \int_{E \leq H(p,q) \leq E + \delta E} \, d\mathbf{p} d\mathbf{q}$$

Quantum Corrections

Thermodynamic state

- The macrostate of the system may be represented by several microstates.
- Microstates (quantum states) can be grouped into energy levels. The number of quantum states for the same energy level is called degeneracy of this energy level.
The Ensemble Average

- $p_i$ is the probability for given ensemble member to be in given state $I$,

$$\bar{F} = \sum_i p_i f_i$$

Internal Energy

$$U = \bar{E} = \sum_i p_i E_i$$

The Microcanonical Ensemble

- System with fixed $N,V,E$
The Microcanonical Ensemble
- System with fixed $N, V, E$
  \[ \Omega(N, V, E), \]
  \[ p_i = \frac{1}{\Omega}, \ E_i = E; \]
  \[ p_i = 0, \ E_i \neq E; \]
  \[ F = \frac{1}{\Omega} \sum_i F_i. \]

The Canonical Ensemble
- System of fixed $N, V, T$

For the states of a system of given $N$ and $V$ in contact with a heat reservoir at temperature $T$, the probability of occurrence of given quantum state is a function of the energy of that state only

\[ p_i = f(E_i) \]
\[ p_{j,k} = f(E_j + E_k) \]

For the large enough ensemble

\[ p_{j,k} = p_j p_k \]
\[ f(E_j + E_k) = f(E_j) f(E_k) \]

The Canonical Ensemble

\[ p_i = A e^{-\beta E_i} \]
The Canonical Ensemble

\[ \sum_i p_i = 1, \]
\[ Q = \sum_i e^{-\beta E_i}, \]
\[ p_i = \frac{1}{Q} e^{-\beta E_i} \]

The Canonical Ensemble Partition Function

\[ Q = Q(N,V,\beta) = \sum_i e^{-\beta E_i} \]

The Grand Canonical Ensemble

- System of fixed \( \mu, V, T \)
The Grand Canonical Ensemble as a collection of Canonical Ensembles

\[ p_i(N) = A(N) e^{-\beta E_i(N)} \]

The Grand Canonical Ensemble

\[ p_N = f(N) \]

The Grand Canonical Ensemble

\[ p_N = A' e^{\gamma N} \]
The Grand Canonical Ensemble

\[ p_{i,N} = p_i(N)p_N = A(N)e^{-\beta E_i(N)}A' e^{-\gamma N} \]

\[ \sum_{i,N} p_{i,N} = 1, \]

\[ \Xi = \sum_{i,N} e^{\gamma N} e^{-\beta E_i(N)} = \frac{1}{\Xi} e^{\gamma N} e^{-\beta E_i(N)} \]

\[ \Xi = \Xi(\gamma, V, \beta) = \sum_{i,N} e^{\gamma N} e^{-\beta E_i(N)} \]
Criteria of Equilibrium

Isolated System

- \( dU = 0, \ dV = 0, \ dN = 0 \)

- \( S \) has its maximum in equilibrium

\[ dS \geq 0 \]

The closed Isothermal system

- \( dT = 0, \ dN = 0, \ dV = 0 \)

- \( F \) has its minimum in equilibrium

\[ dF \leq 0, \]
The closed Isobaric system

\[ dT = 0, \; dN = 0, \; dp = 0 \]

\[ dG \leq 0, \]

\[ G \text{ has its minimum in equilibrium} \]

The open Isothermal system

\[ dT = 0, \; d\mu = 0, \; dV = 0 \]

\[ d\Omega \leq 0, \; \Omega = -pV \]

\[ \Omega \text{ has its minimum in equilibrium} \]

\[ S' = -k \sum_i p_i \ln p_i \]
\[ dS' = -k \sum_i (\ln p_i + 1)dp_i \]

\[ \sum_i p_i = 1; \]

\[ \sum_i dp_i = 0 \]

\[ dS' = -k \sum_i \ln p_i dp_i \]
Isolated system

\[ p_i = \frac{1}{\Omega}, \text{if } E_i = E, \]

\[ dS' = -k \sum_i \ln p_i dp_i = -k \ln \left( \frac{1}{\Omega} \right) \sum_i dp_i = 0; \]

The Closed Isothermal System

\[ p_i = \frac{1}{\Omega}, \]

\[ S' = -k \sum_i \ln \left( \frac{1}{\Omega} \right) \frac{1}{\Omega} = -k \ln \left( \frac{1}{\Omega} \right) = k \ln \Omega \]
\[ F' = \frac{E - S'}{k\beta}; \]
\[ F' = \sum_i \left( E_i p_i + \frac{1}{\beta} p_i \ln p_i \right) = \frac{1}{\beta} \sum_i p_i (\beta E_i + \ln p_i) \]

\[ dF' = \frac{1}{\beta} \sum_i (\beta E_i + \ln p_i + 1) dp_i = \frac{1}{\beta} \sum_i (\beta E_i + \ln p_i) dp_i \]

The Closed Isothermal System

\[ dF' = \frac{1}{\beta} \sum_i (\beta E_i + \ln p_i) dp_i = \frac{1}{\beta} \sum_i \left( \beta E_i + \ln \left( \frac{e^{-\beta E_i}}{Q} \right) \right) dp_i = \]
\[ = \frac{1}{\beta} \sum_i (\beta E_i - \beta E_i - \ln Q) dp_i = -\frac{1}{\beta} \ln Q \sum_i dp_i = 0 \]
The Open Isothermal System

\[ \Omega' = F' - \frac{\gamma}{\beta} \hat{N}; \]

\[ \Omega' = \frac{1}{\beta} \sum_{i,N} p_{i,N} \left( \beta E_i(N) + \ln p_{i,N} - \gamma N \right) \]

\[ d\Omega = \frac{1}{\beta} \sum_{i,N} \left( \beta E_i(N) + \ln p_{i,N} + 1 - \gamma N \right) dp_{i,N} = \]

\[ = \frac{1}{\beta} \sum_{i,N} \left( \beta E_i(N) + \ln p_{i,N} - \gamma N \right) dp_{i,N} \]
Open Isothermal System

\[ d\Omega = \frac{1}{\beta} \sum_{i} \left( \beta E_{i} N + \ln p_{i,N} - \gamma N \right) dp_{i,N} = \]

\[ = \frac{1}{\beta} \sum_{i} \left( \beta E_{i} N + \ln \left( \frac{e^{N e^{-\beta E_{i} N}}}{2} \right) - \gamma N \right) dp_{i,N} = \]

\[ = \frac{1}{\beta} \sum_{i} \left( \beta E_{i} N - \beta E_{i} N + \gamma N - \ln \Xi - \gamma N \right) dp_{i,N} = -\frac{1}{\beta} \ln \Xi \sum_{i} dp_{i,N} = 0 \]

Example

A system has allowed energy states \( E_1=1, E_2=1, E_3=2 \) and \( E_4=2 \). In canonical ensemble representing this system, we find \( E=5/4 \). What is \( \beta \)?

Example

A macroscopic system of given \( N \) and \( V \) has allowed microstates \( E_1=0, E_2=1, E_3=2 \) and \( E_4=2 \). In canonical ensemble with temperature equivalent \( \beta=2 \). What is the probability of occurrence of state \( E_3 \)? What is the energy of macroscopic system?
Example

By use of canonical ensemble obtain derivatives

\[ \left( \frac{\partial E}{\partial V} \right)_{p,N} \text{ and } \left( \frac{\partial F}{\partial P} \right)_{V,N} \]

and show that

\[ \left( \frac{\partial E}{\partial V} \right)_{p,N} + \beta \left( \frac{\partial F}{\partial P} \right)_{V,N} = -P \]