Types of Ensembles

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

The Ensemble Average

- \( p_i \) is the probability for given ensemble member to be in given state \( i \).

\[
\bar{F} = \sum_i p_i F_i
\]
The Microcanonical Ensemble

$$\Omega(N, V, E),$$

$$p_i = \frac{1}{\Omega}, \ E_i = E;$$

$$p_i = 0, \ E_i \neq E$$

The Canonical Ensemble

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

$$p_i = \frac{1}{Q} e^{-\beta E_i}$$

The Grand Canonical Ensemble

$$\Xi = \Xi(\gamma, V, \beta) = \sum_{i,N} e^{\gamma N} e^{-\beta E_i(N)},$$

$$p_{i,N} = \frac{1}{\Xi} e^{\gamma N} e^{-\beta E_i(N)}$$
Criteria of Equilibrium

\[ S' = -k \sum_i p_i \ln p_i \]

\[ F' = \bar{E} - \frac{S'}{k\beta}; \]

\[ F' = \sum_i \left( E_i p_i + \frac{1}{\beta} p_i \ln p_i \right) = \frac{1}{\beta} \sum_i p_i (\beta E_i + \ln p_i) \]
\[ \Omega' = F' - \frac{\gamma}{\beta} \bar{N}; \]

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

Connection between Classical and Statistical Thermodynamics

\[ U = E = \sum_i p_i E_i = \frac{1}{Q} \sum_i e^{-\beta_i} E_i = -\frac{1}{Q} \frac{\partial Q}{\partial \beta_{n,v}}. \]

\[ p = P = \sum_i p_i p = \sum_i p_i E_i \frac{\partial E}{\partial V} = -\frac{1}{Q} \sum_i e^{-\beta_i} \frac{\partial E_i}{\partial V} = \frac{1}{Q} \frac{1}{\beta} \frac{\partial Q}{\partial V_{p,n}}. \]

\[ N = \bar{N} = \sum_{i,N} p_{i,N} N_i = \frac{1}{\bar{Z}} \sum_{i,N} e^{\beta_i} e^{-\beta_i (\bar{N})} N_i = \frac{1}{\bar{Z}} \frac{\partial \bar{Z}}{\partial \gamma_{p,\beta}}. \]

Internal Energy

\[ \bar{E} = \sum_i p_i E_i, \]

\[ d\bar{E} = \sum_i p_i dE_i + \sum_i E_i dp_i, \]
Canonical Ensemble

\[ dE = \sum_i p_i dE_i + \sum_i E_i dp_i , \]
\[ d\bar{E} = -\sum_i \frac{\ln p_i + \ln Q}{\beta} dp_i = \]
\[ -\frac{1}{\beta} \sum_i \ln p_i dp_i = \frac{1}{k\beta} dS' \]

Thermodynamic Functions

\[ dV = 0, dN = 0 \]
\[ dU = TdS , \]
\[ dE = \frac{1}{k\beta} dS' , \]
\[ \frac{1}{k\beta} = T, \]
\[ \beta = \frac{1}{kT} \]

\[ F' = E - \frac{S'}{k\beta}; \]
\[ F' = \sum_i \left( E_i p_i + \frac{1}{\beta} p_i \ln p_i \right) = \frac{1}{\beta} \sum_i p_i (\beta E_i + \ln p_i) = \]
\[ = \frac{1}{\beta} \sum_i p_i (\beta E_i - \beta E_i - \ln Q) = -\frac{\ln Q}{\beta} \sum_i p_i = -kT \ln Q, \]
\[ F = U - TS = E - TS' = E - \frac{S'}{k\beta} = F' \]
Free Energy

\[ F = -kT \ln Q, \]
\[ Q(N,V,T) = \sum_i e^{-E_i/kT}, \]

Internal Energy

\[ \bar{E} = -\frac{1}{Q} \frac{\partial Q}{\partial \beta} = -\frac{\partial \ln Q}{\partial \beta} = kT^2 \frac{\partial \ln Q}{\partial T}, \]
\[ U = kT^2 \frac{\partial \ln Q}{\partial T}_{N,V}, \]
\[ Q(N,V,T) = \sum_i e^{-E_i/kT} \]

Entropy

\[ S = U - F = \frac{kT^2}{T} \frac{\partial \ln Q}{\partial T} + kT \ln Q \]
\[ S = kT \frac{\partial \ln Q}{\partial T}_{N,V} + k \ln Q \]
Pressure

\[ p = -\frac{\partial F}{\partial V}_{N,T} = kT \frac{\partial \ln Q}{\partial V}_{N,T} \]

Grand Canonical Ensemble

\[ dV = 0, \]
\[ dE_{i,N} = dE_{i,N}(V) = 0, \]
\[ \ln p_{i,N} = \gamma N - \beta E_{i,N} - \ln \Xi, \]
\[ E_{i,N} = -\frac{\ln p_{i,N} - \gamma N + \ln \Xi}{\beta} \]

Grand Canonical Ensemble

\[ dE = \sum_{i,N} p_{i,n} dE_{i,N} + \sum_{i} E_{i,N} dp_{i,N}, \]
\[ dE = -\sum_{i,N} \ln p_{i,N} + \ln \Xi - \gamma N dp_{i,N} = \]
\[ \frac{-1}{\beta} \sum_{i,N} \ln p_{i,N} dp_{i,N} + \frac{\gamma}{\beta} \sum_{i,N} N dp_{i,N} = \frac{1}{k\beta} dS + \frac{\gamma}{\beta} d\bar{N} \]
Differential of Internal Energy

\[ dV = 0 \]
\[ dU = TdS + \mu dN, \]
\[ dE = \frac{1}{k \beta} dS' + \frac{\gamma}{\beta} dN, \]
\[ \frac{1}{k \beta} = T, \quad \frac{\gamma}{\beta} = \mu \]
\[ \beta = \frac{1}{kT}; \quad \gamma = \frac{\mu}{kT} \]

Thermodynamic Functions

\[ \Omega' = F' - \frac{\Sigma}{\beta} \bar{S} = F - \frac{\Sigma}{\beta} \bar{S} \]
\[ \Omega = \frac{1}{\beta} \sum_{a} \left( \beta E_{a} + \beta N_{a} + \frac{1}{\beta} \sum_{a} \ln \frac{p_{a}}{\beta} \right) - \frac{1}{\beta} \sum_{a} \left( \beta E_{a} + \ln p_{a} + \gamma N_{a} \right) \]
\[ = \frac{1}{\beta} \sum_{a} \left( \beta E_{a} - \beta N_{a} - \gamma N_{a} - \ln \Xi \right) - \frac{1}{\beta} \sum_{a} \ln p_{a} = -kT \ln \Xi, \]
\[ \Omega = F - \mu N = F' - \mu \bar{S} = F' - \frac{\Sigma}{\beta} \Omega' \]

Grand Thermodynamic Potential

\[ \Omega = -kT \ln \Xi, \]
\[ \Xi = \sum_{i,N} e^{iN/kT} e^{-E_{i}/kT} = \sum_{N} e^{iN/kT} Q(N, V, T) \]
Entropy

\[ S = - \frac{\partial \Omega}{\partial T_{\mu,V}} = kT \frac{\partial \ln \Xi}{\partial T_{\mu,V}} + k \ln \Xi \]

Number of Particles

\[ N = - \frac{\partial \Omega}{\partial \mu_{T,V}} = kT \frac{\partial \Xi}{\partial \mu_{T,V}} \]

Pressure

\[ p = - \frac{\Omega}{V} = \frac{kT}{V} \ln \Xi \]
Example

Consider internal energy of the system in canonical ensemble. Make use of experimental fact that \( C_v > 0 \) to prove that \( k > 0 \).

Fluctuations

Probability to find the system at given energy level

\[ p = \Omega_i p_i = \Omega_i \frac{e^{\frac{E_i}{kT}}}{Q} \]
\[ S = k \ln \Omega_i, \]
\[ \frac{S(E_i)}{k} \]
\[ \Omega_i = e \]

\[ S(E_i) = S(E) + \frac{\partial S}{\partial E}(E_i - E) + \frac{1}{2} \frac{\partial^2 S}{\partial E^2}(E_i - E)^2, \]
\[ S(E_i) = S(E) + \frac{1}{T}(E_i - E) + \frac{1}{2} \frac{\partial^2 S}{\partial E^2}(E_i - E)^2, \]
\[ S(E_i) = \frac{TS(E) - E}{T} + \frac{1}{T} + \frac{1}{2} \frac{\partial^2 S}{\partial E^2}(E_i - E)^2, \]
\[ S(E_i) = \frac{-F(E)}{T} + \frac{E_i}{T} + \frac{1}{2} \frac{\partial^2 S}{\partial E^2}(E_i - E)^2 \]

\[ p = \Omega_i \frac{e^{\frac{E_i}{kT}}}{Q} = \frac{e^{\frac{S(E_i)}{k}}}{Q} \frac{e^{\frac{E_i}{kT}}}{Q} = \]
\[ = \frac{e^{\frac{-F(E)}{kT} + \frac{E_i}{kT} + \frac{1}{2} \frac{\partial^2 S}{\partial E^2}(E_i - E)^2}}{Q} \frac{e^{\frac{E_i}{kT}}}{Q} = \]
\[ = e^{\frac{1}{2} \frac{\partial^2 S}{\partial E^2}(E_i - E)^2} \]
Gauss Distribution Law

\[ p = \frac{1}{\sigma \sqrt{2\pi}} e^{-\frac{1}{2}\left(\frac{x-\bar{x}}{\sigma}\right)^2}, \]

\[ \sigma = \left(\frac{(x - \bar{x})^2}{2}\right)^{1/2} \]

standard deviation

Fluctuations of Energy

\[ \sigma_E^2 = \bar{E}^2 - \overline{E^2}, \]

\[ \overline{E^2} - \bar{E}^2 = kT^2C_V \]

\[ \frac{\sigma_E}{\bar{E}} = \left(\frac{kT^2C_V}{\bar{E}}\right)^{1/2} \propto \left(\frac{1}{N}\right)^{1/2} \]
Thermodynamic Equivalence of Ensembles

\[ \Omega = -kT \ln \Xi, \]
\[ \Xi = \sum_N e^{\beta E / N} Q(N,V,T), \]
\[ \Omega = -kT (\ln Q(V,N,T) + \mu N / kT), \]
\[ F = -kT \ln Q, \]
\[ Q = \sum_i \Omega(E,V,N)e^{\beta E / kT}, \]
\[ F = -kT (\ln \Omega(E,V,T) - \frac{E}{kT}). \]

Example

It is known that for some gas

\[ \Omega(E) = cE^{3N/2} \]

Find internal energy and \( Cv \) of this gas in thermodynamic equilibrium.
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?