Types of Ensembles

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

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

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

Free Energy

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

\[ \bar{E} = -\frac{1}{Q} \frac{\partial Q}{\partial \beta} = -\frac{\partial \ln Q}{\partial \beta} = kT^2 \frac{\partial \ln Q}{\partial T}, \]

\[ U = kT^2 \frac{\partial \ln Q}{\partial T} \]

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

Entropy

\[ S = \frac{U - F}{T} = kT^2 \frac{\partial \ln Q}{\partial T} + kT \ln Q \]

\[ S = kT \frac{\partial \ln Q}{\partial T} + k \ln Q \]

Pressure

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

\[ \Omega = -kT \ln \Xi, \]
\[ \Xi = \sum_{i,N} e^{\mu_N kT} e^{-E_i kT} = \sum_{N} e^{\mu_N kT} Q(N,V,T) \]

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

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

Fluctuations

Probability to find the system at given energy level

\[ p = \Omega_i p_i = \Omega_i \frac{e^{\frac{E_i}{kT}}}{Q} \]
Gauss Distribution Law

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

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

standard deviation

Fluctuations of Energy

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

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

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

\[ F = -kT \ln Q, \]
\[ Q = \sum \Omega(E,V,N)e^{E/kT}, \]
\[ F = -kT(\ln \Omega(E,V,T) - \frac{E}{kT}), \]
\[ \Omega = -kT \ln \Xi, \]
\[ \Xi = \sum Ne^{\muRT}Q(N,V,T), \]
\[ \Omega = -kT(\ln Q(\tilde{R},V,T) - \frac{\muRT}{kT}). \]

Example

It is known that for some gas

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

Find internal energy and \( Cv \) of this gas in thermodynamic equilibrium.
Calculations of Partition Function

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

Classical Approximation

\[ Q(N,V,T) = \int e^{-E(p,q)/kT} \frac{dqdp}{\hbar^n} \]

Shift of the Ground Level of Energy
Complicated Systems

Ideal Monatomic Gas

\[ E = \sum_{i=1}^{N} \frac{p_i^2}{2m} \]

Partition Function of Monatomic Ideal Gas

\[ Q = \left( \frac{V}{\hbar^3} \left( 2\pi m kT \right)^{3/2} \right)^N \]
Thermodynamic Functions of Monatomic Ideal Gas

Entropy of Monatomic Ideal Gas

\[ S = Nk \left[ \ln V + \frac{3}{2} \ln T + \frac{3}{2} \ln \left( \frac{2 \pi m k}{h^2} \right) + \frac{3}{2} \right] \]

Gibbs Paradox
Indistinguishability of the Molecules

\[ Q = \frac{V}{h^3} \left( \frac{2\pi mkT}{h^2} \right)^{3/2} N \]

Entropy of Monatomic Ideal Gas

\[ S = Nk \left[ \ln \frac{V}{N} + \frac{3}{2} \ln T + \frac{3}{2} \ln \left( \frac{2\pi mk}{h^2} \right) + \frac{3}{2} \ln N - \ln 4 \right] = \]

\[ = Nk \left[ \ln \left( \frac{V}{N} \right) + \frac{3}{2} \ln T + \frac{3}{2} \ln \left( \frac{2\pi mk}{h^2} \right) + \frac{5}{2} \ln 4 \right] \]

Validity of Classical Approximation

\[ \Delta p \Delta q \geq \hbar \]
Validity of Classical Approximation

\[ \left( \frac{V}{N} \right)^{1/3} \gg \frac{h}{\sqrt{3mkT}} \]

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?