Equal a priori probabilities

Fundamental Postulate of Statistical Mechanics
for a system at constant \(N, V, E\), all microstates are equally probable at equilibrium

Systems that obey this postulate are deemed "ergodic" - others are "non-ergodic" (e.g., glasses)

E.g., two-state system, 3 slots
\[
\begin{array}{ccc}
\varepsilon = 0 & \varepsilon = 5 & \varepsilon = 25 \\
\hat{1}\hat{0}\hat{0} & \hat{0}\hat{1}\hat{0} & \hat{1}\hat{1}\hat{1}
\end{array}
\]

For any "allowed" microstate \(m\)

\[
P_m = \frac{1}{\Omega(N,V,E)}
\]

For other sets of macroscopic constraints (e.g. const. NVT to be discussed shortly), not all states have the same probability. However, we can always define an "ensemble average" for a property \(x\)

\[
\langle x \rangle = \sum_{m} P_m x_m
\]

Square brackets denote ensemble average.

For ergodic systems, \(\langle x \rangle = \lim_{Z \to \infty} \frac{1}{Z} \int x(t) dt\)

Ensemble average = time average
Maximum Entropy Principle

\[ S(E,V,N | \text{internal constraints}) < S(E,V,N) \]

more microstates possible when internal barriers are removed

Second Law of Thermodynamics: For any spontaneous process in an isolated system, the entropy goes up

\[ S \text{ is maximized at constant } N, V, E \text{ conditions} \]

Conditions of Equilibrium

\[
\begin{align*}
\Delta S & = S_2 - S_1 \\
\text{System 1} & \quad \text{System 2}
\end{align*}
\]

what happens if we bring together systems 1 and 2, allowing them, e.g., to exchange energy?

\[ O_T = O_1 \times O_2 \]

(each microstate of 1 can be coupled with a microstate of 2)

\[ E_1 + E_2 = E_T = \text{constant} \]

The probability of a state of the total system with energy \( E_1 \) is proportional to \( O_T \) consistent with this energy:

\[ P(E_1) \propto O_1(E_1) \times O_2(E_T - E_1) \]
If \( N_1 \) and \( N_2 \) are large, the probability \( P(E_i) \) becomes very sharply peaked - the highest (maximum) probability occurs when

\[
\frac{\partial P(E_i)}{\partial E_1} = 0 \quad \Rightarrow \quad \frac{\partial}{\partial E_1} \ln \frac{P_2(E_i)}{P_1(E_i)} + \frac{\partial}{\partial E_2} (E_2 - E_i) \frac{\partial P_2(E_i)}{\partial E_2} = 0
\]

\[
\Rightarrow - \frac{\partial}{\partial E_2} + \frac{\partial}{\partial E_1} = 0 \quad \Rightarrow \quad \frac{1}{T_2} = \frac{1}{T_1} = \text{condition for thermal equilibrium}
\]

When energy transfer is possible, equilibrium occurs when the temperature of the two systems is equal.

In a similar fashion, if volume or mass could be exchanged between the two systems,

\[
\frac{\partial \ln V_1}{\partial V_1} = \frac{\partial \ln V_2}{\partial V_2} \quad \Rightarrow \quad \frac{\partial \ln V_1}{\partial N_1} = \frac{\partial \ln V_2}{\partial N_2}
\]

\[
\frac{P_1}{T_1} = \frac{P_2}{T_2}
\]

\[
\Rightarrow P_1 = P_2 \quad \Rightarrow \quad T_1 = T_2
\]

[assumes \( T_1 = T_2 \), from energy (thermal) contact]

\[
\begin{align*}
T_1 &= T_2 \\
P_1 &= P_2 \\
T_1 &= T_2
\end{align*}
\]

Conditions of equilibrium

\[
\begin{align*}
T_1 &= T_2 \\
P_1 &= P_2
\end{align*}
\]
Maximization of Entropy at const. \( N, V, E \) implies minimization of Energy at const. \( S, V, N \)

Assume a system with an internal variable \( z \) (e.g. position of a piston)

\[ S(E, V, N, z) \text{ is max } \Rightarrow \left( \frac{\partial S}{\partial z} \right)_{E, V, N} = 0, \quad \left( \frac{\partial^2 S}{\partial z^2} \right)_{E, V, N} < 0 \]

\[ \left( \frac{\partial E}{\partial z} \right)_S = - \left( \frac{\partial E}{\partial S} \right)_S \left( \frac{\partial S}{\partial z} \right)_E = - T \left( \frac{\partial S}{\partial z} \right)_E \Rightarrow \text{If system is at } S \text{ extremum also at } E \text{ extremum} \]

\[ \left( \frac{\partial^2 E}{\partial z^2} \right)_S = \frac{\partial}{\partial S} \left[ - \left( \frac{\partial E}{\partial z} \right)_S \left( \frac{\partial S}{\partial z} \right)_E \right]_S = - \left( \frac{\partial E}{\partial S} \right)_S \left( \frac{\partial^2 S}{\partial z^2} \right)_E \]

0 at \( S \) max

To evaluate this derivative, consider a function \( x(E, z) \)

\[ dx = \left( \frac{\partial x}{\partial E} \right)_S dE + \left( \frac{\partial x}{\partial z} \right)_E dz \]

Take \( z \) derivative at constant \( S \):

\[ \left( \frac{\partial x}{\partial z} \right)_S = \left( \frac{\partial x}{\partial E} \right)_S \frac{\partial E}{\partial z} + \left( \frac{\partial x}{\partial z} \right)_E \]

Let \( x = \left( \frac{\partial S}{\partial z} \right)_E \)

\[ \frac{\partial x}{\partial z} \left( \frac{\partial S}{\partial z} \right)_E = \left( \frac{\partial^2 S}{\partial E \partial z} \right)_S + \left( \frac{\partial^2 S}{\partial z^2} \right)_E \Rightarrow \quad (1) \]

\[ \left( \frac{\partial^2 E}{\partial z^2} \right)_S = - T \left( \frac{\partial S}{\partial z} \right)_E > 0 \quad \text{at extremum} \]
Differential Form

\[ ds = \frac{1}{T} dE + \frac{P}{T} dV - \frac{1}{T} dN \]
\[ dE = Tds - PdV + \mu dN \]

(Entropy representation)

(Energy)

Derivatives of the F.E. determine equilibrium conditions

\[ \frac{\partial E}{\partial S}_{V,N} = T \left( S, V, N \right) \quad \frac{\partial E}{\partial V}_{S,N} = -P \left( S, V, N \right) \quad \frac{\partial E}{\partial N}_{S,V} = \mu \left( S, V, N \right) \]

\( S, E, V, N \) : extensive, prop. to size of system
\( T, P, \mu \) : intensive, independent of size

The F.E. is 1st order with respect to its variables

Euler's Theorem: 1st \[ d \left( Ax, Ay \right) = \lambda \phi \left( x, y \right) \]

Then \[ d = \frac{\partial \phi}{\partial x} x + \frac{\partial \phi}{\partial y} y \]

Proof: \[ d \left( Ax, Ay \right) = \lambda \phi \left( x, y \right) \Rightarrow \frac{\partial \phi}{\partial x} = \frac{\partial \phi}{\partial x} \frac{\partial x}{\partial x} + \frac{\partial \phi}{\partial y} \frac{\partial y}{\partial y} \]

\[ = \phi \left( x, y \right) \Rightarrow x \frac{\partial \phi}{\partial x} + y \frac{\partial \phi}{\partial y} = \phi \left( x, y \right) \]

Applying to \( E \):

\[ E = TS - PV + \mu N \]

Integrated form —

Confusing, appears to have \( T, S, P, V, \mu, N \) as variables?

\[ \Rightarrow T \left( S, V, N \right), P \left( S, V, N \right), \mu \left( S, V, N \right) \text{ are still not independent variables} \]